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HYGRETHERMAL EFFECTS OF EPCXY RESINS AND GRAPHITE/EPCXY COMPOSITES

presented by

JIMING ZHOU

has been accepted towards fulfillment of the requirements for

Ph. D. degree in MATERIALS SCIENCE

James P- Lucay Major professor

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HYGROTHERMAL EFFECTS OF EPOXY RESINS AND GRAPHITE/EPOXY COMPOSITES

By

Jiming Zhou

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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1996

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ABSTRACT

HYGROTHERMAL EFFECTS OF EPOXY RESINS AND GRAPHITE/EPOXY COMPOSITES

By

Jiming Zhou

The aim of this study is to assess the nature of the sorbed water in epoxy resin and related hygrothermal effects in epoxy resins and graphite/epoxy (Gr/Ep) composites. Three neat epoxy resin systems and one Gr/Ep composite were used in this study. Water absorption, desorption, and dimensional variations were investigated. Optical and scanning electron microscopy (SEM and Environmental SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), nuclear magnetic resonance (NMR), and mechanical tests (elastic modulus, strength, failure strain, fracture energy, and fracture toughness) were employed to determine and characterize the effects of water in epoxy resins and Gr/Ep composites.

The claim of two types of bound water, as related to the water-matrix interactions and bonding characteristics, are investigated and indirectly justified by spectroscopy methods in neat epoxy resins. These bonded water states are designated and distinguished as Λ -bonded water and Γ -bonded water. Λ -bonded water is classified as physiosorbed water. Water molecules associated with the Λ -bonded state diffuse into the resin matrix, break the interchain hydrogen bonds which existed initially in the epoxy resin, and form weak hydrogen bonds via Van der Waals forces. Γ -bonded water is suggested as socalled chemisorbed water which interacts with hydrophilic groups of the epoxy resin. The amount of the Γ -bonded water that exists in hygrothermally-exposed epoxy resins depends

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strongly on the immersion temperature and time. In addition, a third type of bound water can exist on the surface and near surface area of Gr/Ep composite. Such bound water state is noted as Θ -bonded water. Θ -bonded water is characterized by its propensity to be retained at surface defects such as cracktips and voids due to surface tension and capillary effects.

Reported in this work is also in the profound effects of sorbed water on the glass transition temperature, T_g . The variation of T_g of epoxy in a hygrothermal environment does not simply depend alone on the water content in epoxy resin. The hygrothermal history of the materials plays a major role in the resultant T_g observed. For a given epoxy system that maintains a constant maximum water content, it was show experimentally that longer exposure time and higher exposure temperature cause higher T_g . T_g is a function of water content, exposure time and temperature, i.e., $T_g = f(\%M, t, T)$. An interpretation based on the bonding characteristics of water molecules and epoxy network is introduced to explain the T_g variation.

Water sorption in epoxy resins and Gr/Ep composites exhibited both Fickian and non-Fickian diffusion behavior. Diffusion data showed that the time for the onset of non-Fickian behavior was inversely related to the exposure temperature. Anomalous (non-Fickian) behavior in the composite resulted from chemical modification and physical damage to the epoxy resin. Cracks, voids, and surface peeling were observed clearly by SEM and optical microscopy. To my wife and son

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I would like to express my sincerest thanks to my advisor Professor James P. Lucas for all of his excellent guidance, friendly manner, and professional example. Without his support and patience this work would not have been possible. I would like to thank Professor Thomas P. Bieler, Professor David S. Grummon, Professor Andre Lee, and Professor David H. Yen for serving on my advisory committee and critically reading the manuscript. Special thanks go to Mr. Michael Rich and the Composite Materials and Structures Center, Michigan State University for providing convenient usage of the facilities for material preparation, sample processing, and property testing.

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LIST OF ABBREVIATIONS AND SYMBOLS

- B_o Magnetic field
- c Moisture Concentration
- c_a Ambient moisture Concentration
- D Mass Diffusivity
- DCB Double Cantilever Beam
- DDA Dicyandiamine
- DDS 4,4'-Diaminodiphenyl Sulfone
- DGEBA Diglycidyl ether of bisphenol-A
- DFT Delamination Fracture Toughness
- DMA Dynamical Mechanical Analysis
- DSC Differential Scanning Calorimeter
- E Potential Energy
- ESEM Environmental Scanning Electron Microscopy
- FTIR Fourier Transform Infrared Spectroscopy
- Gr/Ep Graphite/Epoxy Composites
- h Planck's Constant
- ¹H Proton
- H_z Hamiltonian Operator
- I Spin vector
- ILSS Interlaminar Shear Strength

- Kiv Fracture Toughness
- LSB Laminate Short Bar
- m Spin Quantum Number
- M Magnetization
- M_m Equilibrium Water Content
- M_t Total Percent of Water Gain
- mPDA Metaphenylene Diamine
- NMR Nuclear Magnetic Resonance
- P Angular Momentum
- PAN Polyacrylonitrile
- PMCs Polymer Matrix Composites
- Q Activation Energy
- RH Relative Humidity
- SEM Scanning Electron Microscopy
- TETA Triethylenetetramine
- t Time
- T Temperature
- T_s Glass Transition Temperature
- TGDDM Tetraglycidyl-4, 4'-diaminodiphenyl Methane
- TMA Thermalmechanical Analysis
- UV Ultraviolet
- Ve Volume Fraction of Epoxy
- W Weight of Material
- W_d Dry Weight of Material

- α_{re} Liquid Thermal Expansion Coefficient
- α_{ge} Glassy Thermal Expansion Coefficient
- α. Volumetric Expansion Coefficient of Epoxy
- ρ_{e} Density of Epoxy
- μ Magnetic Moment of Nucleus
- γ Magneto-gyric Ratio
- v Poisson Ratio

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CHAPTERS CONTENT BRIEF

This thesis is organized as follows: Chapter 1 gives a statement of current research status of hygrothermal effects on epoxy resins and epoxy matrix composites and introduces the motivation and objectives of this study. Chapter 2 provides a literature review regarding the nature of water in epoxy resins and the effects of water in epoxy resins and Gr/Ep composites. Experimental water absorption and desorption behaviors in three kinds of epoxy resins are shown in Chapter 3. In this chapter the nature of water in epoxy resin and the bonding characteristics are investigated. In Chapter 4 glass transition temperature variations in different hygrothermal stages are studied. Extensive discussions are conducted regarding the relation of Tg variation and water bonding characteristics in epoxy resins. Swelling, degradation, and mechanical property change of epoxy resins in a hygrothermal environment are presented in Chapter 5. Water absorption behaviors (both Fickian and non-Fickian) in Gr/Ep composites are discussed in Chapter 6. Chapter 7 provides the results of investigations regarding hygrothermal effects on Gr/Ep composites. Finally, conclusions and recommendations are given in Chapter 8.

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CHAPTER I

INTRODUCTION

Owing to their high strength, high dimensional stability, excellent dielectric properties, and light specific weight, polymer matrix composites (PMCs), especially epoxy matrix composites; have for several decades been widely used in space, electronics, and aerospace industries [Lubin 1982, ASM 1988, Springer 1981, 1984, 1988]. In recent years, with significant improvements in processing techniques, manufacturing methods, and cost reduction, applications of graphite/epoxy (Gr/Ep) composites in such commercial markets as automotive components, sporting goods, and marine environments continue to grow.

Like corrosion is for its metallic material counterpart, environmentally induced effects are of major concern for epoxy resins and epoxy matrix composites. Generally environmental factors include temperature, gas (NO_x , SO_x , oxygen etc.), radiation (UV, gamma radiation etc.), moisture, and chemical dissolution [Bank 1995]. Of the most interest are the hygrothermal effects because water or moisture and temperature are the most common of all environmental factors causing performance reduction in polymers and PMCs. Hygrothermal environmental effects of epoxy resins and graphite/epoxy composites have been investigated for a long time for practical reasons [Schutte 1994]. The most prominent amongst the reasons is the fact that sorbed moisture promotes

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material degradation. Some of the physical and mechanical property changes are reversible (plasticization and swelling) and some are irreversible (hydrolysis and microcracking).

In a recent workshop on hygrothermal effects in polymers and polymer matrix composites (sponsored by the National Institute of Standards and Technology, NIST, Gaithersburg, MD, September, 1995), the key topics that were focused on were: i) molecular level understanding of water in polymer and polymer matrix composites, ii) the relationship of sorbed water and macroscopic hygrothermal effects such as plasticization, swelling, cracking, T_g and mechanical property variation, iii) water-induced failure models in composites, especially those associated with the fiber-matrix interface; and iv) long-term physical and mechanical behavior predictions of PMCs.

Although the mechanisms of water in epoxy resin have been widely studied for quite some time, many aspects are still not well understood. A primary issue is the diffusion behavior of water in epoxy resins and PMCs. Some studies on the diffusion of water into resins assumed Fickian behavior. However, there are many examples of non-Fickian-based diffusionm [Weitsman 1995, Zhou 1995, Loos 1981, Imaz 1991]. The ability of these materials to absorb water is another important topic in this field. The water equilibrium level in epoxy resins is influenced by many factors. These include the chemical structure of the resin, the bonding characteristics of water and resin, the matrixfiber interface constraint, microcracking, hygrothermal exposure history, and others.

In general, there are two mechanistic approaches to characterizing water or moisture in epoxy resin and Gr/Ep composite. One is the free volume approach, which presumes that water diffuses into epoxy resin and resides in the available free volume.

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Chemical interaction between water molecules and the epoxy resin is considered insignificant in this approach [Gupta 1985, Woo 1987].

The other approach is the interaction concept, which suggests that water molecules couple strongly with certain hydrophilic groups such as hydroxyls or amines in resin [Moy 1980]. Also Bellenger and Verdu [1989] suggested that water sorption in a polymer resin is essentially governed by water-polymer chemical interactions. The water equilibrium concentrations can be predicted using a simple additive law, depending essentially on the extent of intramolecular hydrogen bonding.

An integrative model has also been developed that considers that some water molecules form hydrogen bonds with hydrophilic groups in the epoxy resin while other water molecules are retained in the free volume in the epoxy resin [Adamson 1980]. Apicella et. al. [1985] proposed a model in which three modes of sorptive behavior exist: i) bulk dissolution of water in a polymer network, ii) moisture absorption onto the surface of holes that define the excess free volume of the glassy structure, and iii) hydrogen bonding between hydrophilic groups of the polymer and water. Jelinski and his collaborators [1985] investigated the nature of the epoxy-water molecule interaction and they showed that: i) the water in epoxy resin is impeded in its movement, ii) there is no free water, iii) there is no evidence for tightly bound water, and iv) it is unlikely that the water disrupts the hydrogen-bonded network in the epoxy resin. The water molecules migrate from site to site, but such a jumping motion does not involve a specific hydrogenexchange mechanism.

Major hygrothermal effects in epoxy systems are primarily plasticization, degradation, swelling, and lowered T_g . Plasticization is the most extensive of all

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hygrothermal effects. Many studies have reported that mechanical property degradation is due to water absorption in epoxy resins and Gr/Ep composites. Investigations have revealed that absorbed water in epoxy acts as a plasticizer [Shen 1981, Imaz 1991, Biro 1993 Lucas 1989, 1993, 1995, Wolff 1993]. The effect of water absorption in Gr/Ep composite is manifested by a reduction in elastic modulus and by a decrease in the matrixdominated strength properties. DeNeve and Shanahan [1993] concluded that the hygrothermal aging of epoxy leads to both plasticization of the polymer (a physical effect) and chain scission (a chemical effect).

Although it is widely accepted that ~1% of sorbed water may decrease T_g by 10-20 °C, the interpretation for the decrease in T_g is varied. Based on the free volume concept of polymeric materials, many studies have shown that T_g change simply depends on water content of the resin [Kelley 1960, Browning 1978, Cairns 1984]. DeIasi [1978] suggested that water which disrupts the interchain bonds could depress T_g , whereas, water that forms clusters or hydroxy-water type groupings has no measurable effect on T_g . Mijovic [1985] reported that T_g was also influenced not only by water concentration but also by exposure temperature.

Swelling denotes volumetric dimensional change due to moisture content alone, independent of thermal expansion. Hahn [1976] showed that the sorbed water produces relatively little swelling until a critical amount of water is absorbed, and then the resin sample volume increases proportionally to the additional water content. Adamson [1980] considered the swelling coefficient of water absorbed to be temperature and concentration dependent. Sorbed water molecules may either occupy free volume (causing no swelling), or interrupt interchain hydrogen bonding (causing swelling).

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Although there is some general agreement among some models, considerable disagreement still persists. The key point is the nature of water in epoxy resin. The problem is if water stays in the material in the form of bulk or cluster, or bonded with hydrophilic groups, or separating in free volume. Since there is no enough knowledge on the basic behavior of water in epoxy resin the interpretation on plasticization, swelling, and degradation is varied. This is due in part to the reality that the hygrothermal effects, as a consequence of moisture absorption in polymers and PMCs, are chemically and mechanically complex. The other reason is that most of the previous scientific investigations did not apply correlated integral spectroscopic methods and mechanical testing to explore the effects of water in epoxy resin systems. Usually only one or two probing methods were employed to yield some results. Consequently there is no single theory with sufficient experimental support to explain all related phenomena of moisture behavior in epoxy resins and epoxy matrix composite systems.

The aim of this study is to discern the effects and bonding characteristics of sorbed water in epoxy resin and Gr/Ep composite by evaluation of: i) water absorption and desorption phenomena in epoxy resin and Gr/Ep composites, ii) sorption mechanisms of water in epoxy resin, iii) plasticization and glass transition temperature modifications for both epoxy resin and Gr/Ep composites, iv) moisture induced swelling, and v) mechanical property variations in different hygrothermal exposure conditions.

The materials used in this study involve three kinds of epoxy resins and one Gr/Ep composite. One epoxy resin is diglycidyl ether of bisphenol-A (DGEBA, Shell Epon828) and metaphenylene diamine (mPDA) epoxy system. The second is tetraglycidyl-4, 4'- diaminodiphenyl methane (TGDDM, Ciba Geigy My720) resin with 4,4'-diaminodiphenyl

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sulfone (DDS, DuPont) hardener. The third is Fiberite 934 epoxy system which consists mainly of TGDDM and DDS with small amounts of other additives of which the types and their concentrations are proprietary. The three kinds of epoxies have been used extensively for high performance polymer matrix composites. The Gr/Ep composite is Fiberite T300/934 unidirectional laminate.

In this study water absorption, desorption, and dimensional change measurements were carried out. Optical and electron microscopy (SEM and Environmental SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermomechanical analysis (TMA), nuclear magnetic resonance (NMR), and mechanical test (tensile, flexural, fracture energy, and fracture toughness) were employed to determine and characterize the properties and effects of water in epoxy resins and Gr/Ep composites. Using an integrative experimental approach, a more comprehensive understanding of the nature of water and the hygrothermally induced effects in epoxy resin and epoxy matrix composites has emerged.

CHAPTER II

LITERATURE REVIEW

In this chapter we will review the literature on the nature of water in epoxy resin and the hygrothermal effects in epoxy resins and Gr/Ep composites. The sorption of water in PMCs and their effects on composite performance are highly complex issues. Their study involves, in the least, the disciplines of polymer science and applied mechanics, where the former focuses on molecular-level interactions and the latter is concerned with mechanical response. A historical perspective of hygrothermal effects investigation can be found in several review articles [Weitsman 1995, Lee 1993, Bank 1995, Wolff 1993, Schutte 1994]. The kinetics of water sorption in polymer has been studied for about one and a half centuries, perhaps beginning with Fick [Weitsman 1995].

Before high performance PMCs were widely used in aerospace industry, hygrothermal effects were considered to be of only secondary importance. Glass fiber composites, for example, were utilized in the boating industry. While such composites exhibit substantial sensitivity to water, these detrimental effects were overcome by overdesign, with lesser concern for any possible waste in weight or performance. With the application of tight design requirements and high performance polymer matrix composites, especially Gr/Ep composites applied in aerospace industry, the interest in water sorption and its effects on polymers received new impetus in the mid 1970s. The first wave on the study of hygrothermal effects of high-performance PMCs came about in the late 1970s and early 1980s. Springer's three volumes of collective works [Springer 1981, 1984, 1988] represented the studies of that period. In the late 1980s, the issue was relatively quiet. With the quick development of the applications in the use of PMCs, the second wave came about in the 1990s. It appears that the wave of interest in environmental effects on PMCs may be due to new applications contemplated for these materials, which combine severe exposures and tighter design requirements. These new applications occur in the offshore oil industry, in naval submersibles, and in the automotive industry. This time research has focused on molecular level interactions of water with polymers and the mechanical response of water-sorbed PMCs [Cappelletti 1995, Etxeberria 1995, Karasek 1995, Rao 1995, Lucas 1995].

2.1. THE STRUCTURE OF EPOXY RESIN AND EPOXY COMPOSITES

2.1.1. Polymers

The fundamental difference between polymers and other classes of materials is derived from their linear-molecular nature. Although polymers may be connected by crosslinking, their basic structure consists of a linear repeating pattern of strong bonds, in contrast to the three-dimensional structures associated with metal and ceramics. The consequence of this fundamental difference in bonding is that many of the mechanical properties depend on the weaker forces between the chains, in addition to the primary covalent bonds along the main chain axis. Without entanglement or some other forces holding chains together few useful mechanical properties would develop. Consequently, polymers are susceptible to thermal effects at relatively low temperatures. Their properties largely reflect the lower magnitude of these secondary forces holding the polymer chain together. This constitutes a great manufacturing advantage because it allows processing at modest temperatures. This has led to a rapid increase in the use of polymeric materials, and it provides a driving force to better understand the influence of temperature, moisture, and other environmental variables on the final properties, since water molecules and relatively modest temperatures and can disrupt the secondary force. Also, minor changes in the number of covalent bonds along a chain have an enormous effect on the molecular weight and, hence, the mechanical properties.

There are two important concepts on polymeric materials, which can help us better understanding the behavior of water in epoxy resins. One is "occupied volume" and the other is "free volume". Occupied volume is defined as that volume occupied by the actual mass of a molecule plus the volume it occupies because of thermally dependent harmonic vibration that excludes all other molecules from its domain. Occupied volume is dependent on temperature because thermally induced motion causes each molecule (or molecular segment in the case of a cross-linked polymer) to move about its equilibrium position, therefore occupying more space than its actual mass volume. If the molecules were packed so that their domains were in perfect contact, the occupied volume of the polymer at any temperature would exactly equal the sum of the actual mass volume of the molecules and their vibrational volume. The domain are not in perfect contact, however, and free volume is defined here is the difference between the measured volume of a polymer and the occupied volume. This difference is the result of "holes" or "voids" caused by packing irregularities. A critical free volume fraction at T_g for most polymers is about 1/40 (2.5 \pm 0.3%) of the total volume occupied by the substance [Adamson 1980].

The useful mechanical properties of polymers result from the high molecular weight of the chains. In a highly cross-linked form, an infinite molecular weight is reached and a classification according to the mean molecular weight between crosslinks is more applicable. The types of bonds that hold the polymer together are listed in table 2.1. The strongest are covalent bonds along the main chain of the polymer, while much weaker bonds exist between the repeat units of the polymer. These secondary interactions are repeated sequentially many times and lead to substantial strengthening. In addition, there are the related frictional forces that restrict the ability of chains to untangle when a polymer is deformed.

2.1.2. Epoxy

By definition, any resin containing the molecular group $-\overset{\vee}{\underset{\Gamma}{}}_{-\overset{\vee}{}}$ is called epoxy resin. Epoxy is one of the polymeric materials and the resins provide the highest adhesive strength of any known polymeric material. Epoxies can thoroughly wet a wide variety of substrates with minimal shrinkage. Epoxy resins can be used to join many dissimilar materials and to form excellent-property composites.

The epoxy group can bond chemically with other molecules, forming a large threedimensional network. This process, called curing, changes a liquid resin into a solid. The most commonly used curing agents are aromatic and aliphatic amine curing agents (hardeners). Each hardener molecule contains a reactive group on each end. These permit the formation of a crosslink between epoxy molecules. An amine end-group with two hydrogens on the nitrogen (a primary amine) reacts with an epoxy molecule as follows:

$$\begin{array}{ccc} O & OH \\ / \ \\ H_2N & ----NH_2 + H_2C - CH & ----- \\ H_2N & ----NH - CH_2 - CH & ----- \\ \end{array}$$

When another amine hydrogen combines with a second epoxy molecule, crosslink is formed:



After thorough crosslinking, epoxy reaches almost infinitive molecular weight and forms a brittle and stiff solid. The carbon-nitrogen bond formed in crosslinking is stable against most inorganic acids and alkalis.

Table 2.1 Types of bonds and their strength in polymer [Atkins 1993]



2.1.3. Graphite Fibers

Carbon fibers are by far the predominant high-strength, high-modulus reinforcing agent currently used in the fabrication of high-performance resin-matrix composites. The crystallographic structure of a perfect single crystal of graphite is shown in part (a) of Fig. 2.1. As can be seen, the graphite crystal is composed of many sheet-like layers of the carbon atoms which are stacked one on top of the other and separated by a distance of 3.35 Å. In the plane of the sheets, the carbon atoms are linked together by very strong covalent bonds. As a result, the theoretical tensile modulus of elasticity and ultimate tensile strength of the crystal in a direction parallel to the basal plane are very high — on the order of 1000 GPa and 15 GPa, respectively. On the other hand, relatively weak Van der Waals bonds hold the sheet-like layers of carbon atoms together in a direction normal to the basal plane; consequently, the mechanical properties of the crystal in this direction are much poor. In a graphite fiber, the structure of the crystallites is not that of the perfect single crystal. Instead, the stacking arrangement of the various carbon sheet is slightly displaced, thus forming a "turbostratic" graphite shown in part (b) of Fig. 2.1. The orientation of the graphite sheets, however, is still more or less parallel to the fiber axis.



Fig. 2.1 Crystallographic structure of (a) graphite and (b) turbostratic graphite [Lubin 1982].

The current technology for producing graphite fibers generally centers on the thermal decomposition of various organic precursors. Commercially available graphite fibers are made using one of three precursors: rayon, polyacrylonitrile (PAN), and pitch. For example, the process by which PAN is converted to carbon fibers involves seven steps:

- 1. Spinning the PAN precursor.
- 2. Stretching the precursor.
- 3. Stabilization at 220 °C in air under tension.
- 4. Dehydrogenation at 400-600 °C.
- 5. Denitrogenation at 600-1300 °C.
- 6. Carbonization at 1500 °C in inert atmospheres.
- 7. Graphitization at 1800 3000 °C in inert atmospheres.

The chemical structure of PAN is shown in part (a) of Fig. 2.2. Part (b) of Fig. 2.2 is the structure of the stabilized PAN. Figure 2.3 shows the mechanism for the formation of graphite ribbons in PAN fibers. Carbonization heat treatments are generally carried out in an inert atmosphere at temperatures ranging from 1000 °C to 1500 °C. It is within this temperature range that most noncarbon elements are driven the precursor fiber. At temperature less than 1000 °C, a considerable amount of gaseous products, such as methane, hydrogen cyanide, water, carbon dioxide, carbon monoxide, hydrogen, and various other hydrocarbons, are evolved from the precursor fiber. The chemical composition of the fiber at 1000 °C is approximately 94% carbon and 6% nitrogen. At 1300 °C the nitrogen content of the fibers is approximately 0.3%. In general, graphitization heat treatments are specifically carried out at temperatures in excess of

1800 °C in order to improve the tensile modulus of elasticity of the fiber by improving the crystallite structure and the preferred orientation of the graphite-like crystallites within each individual fiber. Graphite fibers have a more highly organized three-dimensional crystalline structure than non-graphitized carbon fibers. Therefore graphite fibers have higher moduli and strength and are better thermal conductors than carbon fibers.

Graphite fibers are subjected to post treatment (including surface treatments an/or application of organic sizings) in order to improve their compatibility with the resin matrix and/or their handleability. The mechanical properties, including flexural strength, interlaminar shear strength (ILSS), and mode of fracture, of a graphite-fiber-reinforced







Fig. 2.2 Structure of PAN fiber. (a) original PAN and (b) stabilized PAN fiber through oxidization [Lubin 1982].

composite depend on the nature of the resin-fiber bond. Organic coatings (sizings) in an amount of 0.5 -7 wt% typically applied by the manufacturer by passing the heated fibers through a sizing bath. The sizing agents most commonly employed are polyvinyl alcohol, epoxy, polyimide, and water. These coatings are applied to both untreated and surface-treated fibers. They not only improve the handleability and abrasion resistance of the fibers, but also affect their adhesion to the matrix.



Fig. 2.3 The mechanism for the formation of graphite ribbons in PAN fibers.

2.1.4. Graphite/Epoxy Composites

The main resins used in high performance fiber composites are thermosetting polymers that can be used at high temperatures. Thermoplastic polymers are used to a lesser extent because they are subject to changes in modulus and strength with temperature, solvent resistance is often poor, and high melt viscosity makes fiber wetting and infiltration difficult.

Graphite/epoxy composites consist of graphite fibers embedded in an epoxy matrix. The graphite fibers provide stiffness and strength while the epoxy matrix distributes the stress to and among the fibers and holds them together. Gr/Ep composites have higher tensile moduli, tensile strength, and much lower density than metal.

2.2. WATER TRANSPORT IN EPOXY RESIN

2.2.1. Absorption Kinetics in Epoxy Resin

A problem in which the temperature and moisture distributions inside the material are to be determined is frequently referred to as the "moisture problem". It is required to find the following parameters:

1) the moisture concentration inside the material as a function of position and time,

2) the total amount of moisture as a function of time, and

3) changes in the "performance" of the material as a function of time.

Answers to problem involving changes in performance (point 3) must be obtained by testing. Answers to the point 1 and 2 can be obtained by analytical means when the following conditions are met. 1) The temperature inside the material approaches equilibrium much faster than the moisture concentration, and hence the energy (Flourier) and mass transfer (Fick) equations are decoupled.

2) The moisture diffusion can be described by a concentration-dependent form of Fick's law.

3) The thermal conductivity and the mass diffusivity depend only on temperature and are independent of moisture concentration or of the stress levels inside the material.

When all the foregoing assumptions are satisfied the diffusion process is said to be "Fickian". Appropriate equations and solution procedures are given in Chapter 3.2.1 for calculating temperature and moisture distributions in case of Fickian diffusion.

The behavior of water in epoxy resin is highly complex. Moisture absorption and desorption at high temperatures and relative humidity can cause voids and/or microcracks in the epoxy resin. If these effects are extensive, conditions for non-Fickian transport can be induced, Thus, we can expect non-Fickian as well as Fickian transport, according to the resin properties and environmental conditions. But it is still not well understood that for a given epoxy resin, some studys show physical damage and some studys do not observe any cracking and/or microvoids. The diverse results may be associated with difference in sample preparation and in chosen experimental procedures.

Brewis et al. [1980] investigated water sorption kinetics of the diglycidyl ether of bisphenol A cured with several kinds of hardener. They found that the water sorption behavior of all the samples followed a Fickian diffusion model in the temperature range from 25 to 100 °C. Similar results in PMCs have been reported by Rao [1995]. He studied moisture diffusion characteristics of T300/914C unidirectional composite specimens hygrothermally conditioned at 85% RH and 70 °C. All the test specimens exhibited Fickian diffusion behavior. He concluded that for well-fabricated, void-free composites, the Fickian diffusion model is valid [Rao 1984, 1995].

Several researchers [Moy 1980, Wong 1985, Sahlin 1991] have reported non-Fickian diffusion in tetraglycidyl 4,4'-diamino-diphenylmethane (TGDDM) resin cured with DDS. Moy and Karasz [1980] suggested that such an effect is coupled either to relaxation processes or to irreversible chemical reactions. They proposed that the water interacted with the polymer through hydrogen bonding, as verified by differential scanning calorimetry. They showed that the residual water could only be removed from the resin by exposing it to a dry atmosphere heated above 100 °C. Wong and Broutman [1985] concluded that the non-Fickian process observed during a first sorption cycle may be due to insufficient crosslinking. Additional crosslinking could potentially occur during this sorption process. They observed Fickian behavior for subsequent sorption cycles. Sahlin and Pepas [1991] found that TGDDM/DDS resins exposed to water at 25 °C showed non-Fickian behavior. They explained that this behavior can be exhibited when the relaxation phenomena are of the same order of magnitude of time scale as diffusion. The non-Fickian behavior observed in the water uptake curves at low sorption times for samples exposed to water at 25 °C disappeared as the sorption temperature increased. Shirrell [1977] found non-Fickian absorption anomalies for both postcured and non-postcured T300/5208 composite exposed in moisture at 82 °C. The equilibrium moisture solubility of non-postcured specimens are independent of testing temperature, while there is a definite trend toward lower equilibrium moisture content with increasing test temperature

for postcured specimens. Loos (1981) observed both Fickian and non-Fickian absorption process in glass fiber reinforced composites and gave a plausible explanation. Moisture rapidly entered the material and caused microcracks. As the cracks developed, material, most likely in the resin particles, was actually last. As long as the moisture gain was greater than the material loss, the weight of the specimen increased. Once the weight of the lost material exceeded the weight of the absorbed water, the weight of the specimen decreased. This is a very good prediction but there was no further experiment to support it. Zhou and Lucas [Zhou 1995] studied the diffusion behaviors of Fiberite 934 resin and Fiberite T300/934 composite systematicly and reported the diffusion is Fickian. The anomalous diffusion profiles are just due to material surface cracking and mass loss.

Some researchers [Loos 1979, Illinger 1980, Wright 1981] showed that sorption behavior tends to occur in two stages. Whitney and Browning [1978] observed a twostage diffusion process in Hercules 3501-5 resin at 71 °C. They suggested time-dependent matrix cracking as the mechanism associated with the two-stage diffusion process. Gupta et al. [1985] found that the DGEBA resin cured with metaphenylenediamine showed Langmir-type sorption behavior at room temperature while, at higher temperatures, Henry's Law mode was more relevant. The Langmurian mode involes the entry of water molecules into preexisting gaps while in the Henry's Law mode; the water molecules enter through gaps created by segmental motion. Carter and Kibler [Carter 1978] suggested a Langmuir-type model to predict two-stage sorption behavior for composite resins. The model could fit anomalous uptake curves for 5208 resin exposed to several relative humidities. From the fact that the same parameters give equally good fits to the data at all humidities, they suggested that the absorption anomaly does not result from non-linear effects.

Studies over the last two decades have revealed some general results: the moisture transport in composites can be described by a Fickian diffusion model with a constant diffusion coefficient [Shen 1976, Loos 1979, Illinger 1980, Boll 1985], a concentrationdependent diffusion coefficient [Shirrell 1978], or a stress-dependent diffusion coefficient. Weitsman [Weitsman 1995] summarized the effects of fluids on PMCs and gave six possible water gain profiles: 1) Fickian diffusion curve, 2) a curve corresponds to the often encountered circumstance of a continuous gradual increase in weight gain, 3) a curve represents the so-called "two-stage diffusion" behavior, 4) a curve is sometimes associated with a moving diffusion front, 5) a curve corresponds to a rapidly increasing moisture content within the composite, which is usually accompanied by large deformations, damage growth, material breakdown, and 6) a curve accords with weight-loss that is attributable to irreversible chemical or physical break-down of a material. Most commonly, weight-loss occurs in conjunction with hydrolysis, or the separation of side group from the polymeric chains, or the dissociation of matter located at the vicinities of fiber/matrix interfaces. Zhou and Lucas [Zhou 1995] also suggested six types of potential water uptake profiles. The result are similar with Weitsman's except the case 4 because it is associated with water-vapor induced corrosion of glass fiber. Graphite fiber is water impermeable and does not has this behavor. The detail is in Chapter 6.

2.2.2 Mechanism of Water Absorption

It is very important to know the nature of water in epoxy resin at the molecular level because that fundamental knowledge is useful for us to understand and explain the

salient aspects of hygrothermal phenomena. Although the mechanism of water absorption has been investigated from the initial stage of the hygrothermal effect, to date, the state of understanding is still incomplete. Adamson [1980] investigated thermal expansion and swelling by using epoxy resin Hercules 3501-5 and Gr/Ep composites Hercules AS/3501 and Fiberite T300/934 prepreg. He suggested that some water molecules form hydrogen bonding with hydrophilic groups in epoxy resin while other water molecules are retained in free volume of the epoxy resin. Apicella et al. [1983] studied the water sorption modes of glassy epoxy resin DGEBA cured with TETA and TGDDM cured with DDS and proposed that there are three absorption modes: (1) bulk dissolution of water in the polymer network, (2) moisture absorption onto the surface of vacuoles which define the excess free volume of the glassy structure, and (3) hydrogen bonding between polymer hydrophilic groups and water. If the first two modes occur consecutively, a dual sorption behavior can be determined. Antoon et al. [1981] showed that the frequency of the inplane bending mode of sorbed water in epoxy resin lies between its frequency in liquid and free (gaseous) water, another indication of hydrogen bonding. Browning Browning 1983] proposed that absorbed water molecules can be combined with a functional group of a highly polar nature in cured epoxy resins as follows:



Jelinski and collaborators [Jelinski 1985] investigated the nature of the epoxywater molecule interaction using quadruple echo deuterium NMR spectroscopy. They revealed that (1) the water in epoxy resin is impeded in its movement, (2) there is no free water; (3) there is no evidence for tightly bound water; and (4) it is unlikely that the water form disrupts the hydrogen-bonded network in the epoxy resin. The water molecules migrate from site to site, but such a jumping motion does not involve a specific hydrogenexchange mechanism. Using dielectric experiments, Woo and Piggott [Woo 1987] suggested that the water does not appear to be bound to polar groups in the resin or hydrogen bonding sites. They reported that there was only some clustering of water molecules in the polymer, rather than complete molecular separation.

Joncock and Tudgey [1986] found that water absorption depends on the amount of free volume in the polymer network. They showed that the contribution of polar groups in terms of their hydrogen bonding capabilities is reflected by the effect of metachloro, bromo, and methyl substituents on the water absorption of the modified DGEBA epoxy resins cured with DDS hardener, while substituents in the ortho position adversely affect the hydrogen bonding capabilities of amine groups and limit the extent of reaction by steric interference. Also by using O-glycidyl resin systems cured with various amounts of DDS hardener, they proved that free volume plays an important part in determining the level of water absorption.

2.3 HYGROTHERMAL EFFECTS ON EPOXY AND GR/EP COMPOSITES

2.3.1 Plasticization and T_g Variation

The hygrothermal effects of absorbed water in epoxy systems are mainly plasticization, degradation, swelling, and lowered T_g . Plasticization is the least controversial issue in all hygrothermal effects. Many works reported mechanical property degradation due to water absorption in epoxy resins and Gr/Ep composites. T_g variation has also been studied intensively. Investigations have revealed that absorbed water in epoxy acts as a plasticizer [Shen 1981, Imaz 1991, Biro 1993, Lucas 1993, Wolff 1993]. The effect of water absorption in Gr/Ep composite is manifested by a reduction in elastic modulus and by a decrease in the matrix-dominated strength properties. Although the basic result that 1% of sorbed water may decrease T_g by 10-20 °C is widely accepted, interpretation of the T_g decrease is varies.

Based on the free volume concept of polymeric materials, Kelley and Bueche [1960] derived the following expression for the Tg of a plasticized system:

$$T_g = \frac{\alpha_p v_p T_{gp} + \alpha_d (1 - v_p) T_{gd}}{\alpha_p v_p + \alpha_d (1 - v_p)}$$

Here, α is the expansion coefficient, v is the volume fraction, and subscripts p and d represent polymer and diluent, respectively. This is a classical method for predicting the variation of T_g in water-sorbed resin. Several investigators [Cairns 1984, Browning 1978] applied this equation to epoxy resin/water system and explained the dependence of T_g on water content.

Couchman and Karasz [1978] extended the classical thermodynamic treatment of composition-dependent T_g originally proposed by Gordon et al. [1977] Karasz and

coworkers [Brinke 1983, Ellis 1984] modified the equation to apply it successfully to epoxy resin/water systems. DeIasi [1978] suggested that water which disrupts the hydrogen bond could depress T_g , whereas, water that forms cluster or hydrogen-water type groupings has no measurable effect on T_g . Other experimental data [Apicella 1979, McKague 1978, DeNeve 1993, Bellenger 1989] have shown that the T_g of epoxy resins or Gr/Ep composites generally decreases as the water content increases.

Mijovic and Weinstein [1985] found that the depression of the glass transition temperature in a Gr/Ep composite after water absorption is strongly dependent on the temperature of the environment during water absorption. At the same absorbed water content, the T_g depression was greater at higher absorption temperature. They concluded that at lower temperatures, the temperature dependence comes from the water that exists predominantly in the defects at the interface and, to some extent, in the lower crosslink density matrix, while, at a higher temperature, it comes from water penetrating into the highly crosslinked regions within the resin. Zhou and Lucas [Zhou 1994] found that T_g does not simply depend on water content. The T_g value of a hygrothermally exposed epoxy resin depends on its exposure history. Longer exposure time and higher exposure temperature induce higher value of T_g . These results are quite different from Mijovic's results. The detailed discussion can be found in Chapter 4 of this dissertation.

2.3.2 Change of Mechanical Properties

Water absorption causes resin plasticization concurrently with swelling and lowering of its T_g . These effects usually accompany modulus changes of the material. Shen and Springer [1977] summarized the previous tensile modulus data of composites and concluded that for 0° and $\pi/4$ laminates, there appears to be very little change in the

bulking moduli over the entire spectrum of water contents from dry to fully saturated in the temperature range of 200 to 450 K, whereas, for 90° laminates, the saturated moduli decreased considerably with increases in both the water content and temperature.

Using the stress-strain data of various water-treated samples of neat resin and composites, Browning et al. [Browning 1978] conclude that, as water absorption increased and/or as temperature increased, the tensile modulus of the resin matrix and the transverse modulus of the composite decreased. Crossman et al. [Crossman 1978] determined the tensile relaxation modulus after exposure to equilibrium moisture levels. They found drastic reductions in modulus and an enhanced rate of relaxation at higher temperatures and moisture contents.

Dynamic mechanical tests of epoxy resins have been used to investigate the change of molecular structure for various epoxy resin curing agent systems [Chu 1984, Apicella 1979, Kuzenko 1980, Mikols 1982] and to study hygrothermal effects on their molecular structure [Kuzenko 1980, Mikols 1982, Chu 1984]. They have also been applied to reinforced epoxy composites to investigate the effects of reinforcement [Mikols 1980, Lee 1989] and hygrothermal effects [Dynes 1979].

Kuzenko et al. [1980] investigated the dynamic material properties of TGDDM epoxy resins cured with DDS curing agent and boron trifluoride catalyst. They observed a glass transition around 234 °C; the width of the glass transition peak was proportional to the cyclic "viscosity" of the sample. They observed that a sample containing 6.4 wt% water exhibited a significant plasticizing effect in the dynamic shear modulus vs. temperature curve. They also showed a shift towards lower values and a broadened peak of the glass transition. The nature of the interface region between matrix and fiber in a composite influences its mechanical properties. Spathis et al. [1984] prepared an epoxy matrix/fiber specimen and an epoxy matrix/silane-coated fiber specimen and compared the response of their dynamic mechanical properties. They found that a specimen that had weaker interfacial bonding showed lower values of storage and loss moduli and higher values of damping factor. Chua [Chua 1987] characterized the quality of the interfacial adhesion by the value of the damping factor at the T_g . He observed that the dynamic modulus at the T_g of the glass fiber-reinforced polyester resin increases when the amount of unreacted organosilane at the interface is increased. Banerjee et al. [Banerjee 1990] reported that the poor interfacial bonding in the untreated fiber specimens led to a large viscous dissipation at the carbon-epoxy interface and that because of a weak interface the T_g of the untreated fiber specimen was slightly lower than that of the surface-treated fiber specimen.

2.3.3 Swelling Induced by Absorbed Water

Swelling denotes volumetric dimensional change due to moisture content alone, independent of thermal expansion. Since water is polar, it is capable of forming hydrogen bonds with hydroxyl groups. Therefore, interchain hydrogen bonds can be disrupted to increase the intersegmental hydrogen bond length [Kwei 1966]. Rehage and Borchard [1973] showed that water can combine with polymers in the glass state, establishing an equilibrium between the liquid and glass state.

Adamson [1980] considered the swelling efficiency of sorbed water to be temperature and concentration dependent. Sorbed water molecules may either occupy free volume causing no swelling or interrupt interchain hydrogen bonding causing swelling. Kong and Adamson [1983] also showed the increase in the partial volume of the water experimentally. Hahn [1976] showed that the absorbed water produces relatively little swelling until a critical amount of water is absorbed, and then the resin sample volume increases proportionally to the additional water content. Moisture absorption in the fiber (i.e., carbon fiber) is negligible. Therefore, Hahn [Hahn 1976] suggested that the transverse swelling strain of the composite could be calculated using:

$$\varepsilon_t = [(1+\nu_m)/3]d(M-M_o)$$

where

$$M_o = V_o/d = v_m d_m M_{mo}/d$$

Here, ε_t is the swelling strain in the transverse direction, v_m is the matrix Poisson's ratio. M is the moisture concentration, M_o is the minimum value of M at which swelling is observed, V_o is the volume fraction of voids, d is the total specific gravity, and d_m is the matrix specific gravity.

DeNeve and Shanahan [1993] used DGEBA and dicyandiamine DDA resin system and concluded that the hygrothermal aging of epoxy leads both to plasticization of the polymer (a physical effect) and chain scission (a chemical effect). Cairns and Adams [1984] showed that the moisture-induced linear strain of such an epoxy resin exhibits a linear relation proportionally with the amount of absorbed moisture. Gazit [1978] showed that the weight increase of moisture was proportional to the linear dimensional change and was the same for all samples having the same reinforcements at all levels of ambient humidity.

2.3.4 Hygrothermal Degradation in Epoxy Resin and Gr/Ep Composites

Degradation of composite materials in structural applications may be caused not only by mechanical loading but also by environmental exposure. Most of the environmental degradation in composites is due to their exposure at increased temperature and to humidity. The absorbed water not only plasticizes the matrix resin, but it can also change the state of residual stresses to cause microvoids and/or microcracks in the resin [Wright 1980, Apicella 1979, Shirrell 1978]. Some researchers [Farra 1978, Dewimille 1983] observed hygrothermally induced cracks in the bulk epoxy resin regions of glass fiber/DGEBA epoxy composites as well as at the interface of the glass fiber and DGEBA epoxy resin. Browning [1978] reported that one significant mechanism for the loss of elevated temperature properties in a moisture-rich environment is the formation and growth of cracks in the material where the crack growth process is aided by localized chemical chain scission at the crack tip. He also found that microcracking increases the equilibrium moisture absorption level.

Shirrell et al. [1979] exposed T300/5208 composite samples to several different hygrothermal environments and examined the hygrothermally induced microcracks by scanning electron microscopy (SEM). They found that severe microcracks were observed at 82 °C and that the severity and frequency of these microcracks increases with relative humidity. They also found that postcured specimens generally formed more severe microcracks than identically exposed non-postcured specimens.

Morgan and Mones [1980] concluded that sorbed moisture enhances the craze cavitation and propagation processes in amine-cured epoxy resins, whereas the initial stages of failure enhance the accessibility of moisture to sorption sites within the epoxy to a greater extent than in the later stages of failure, which involve crack propagation alone. Hahn [1987] explained that the hygrothermal degradation is the result of matrix plasticization, microvoid formation, and microcracking. Apicella and Nicolais [1985] also observed a Langmuir-type, two-step moisture diffusion in epoxy resins due to the moisture-induced microcavities. Halpin [1985] observed that the rate of the apparent diffusion process and the magnitude of the equilibrium weight gain are accelerated by the presence of cracks and voids in a laminate.

Leung and Kaelble [1980] predicted that the possible microcracks and delaminations within the composite due to the stress gradient are caused by the moisture content gradient. Fedors [1980] found that some inclusions in epoxy resin systems can be dissolved to form cavities when the diffused water reaches the surface of the inclusions. The difference in the chemical potential of the water in the pure state and in solutions, which manifests itself as an osmotic pressure, tends to make the initially concentrated solution in the cavity more dilute. He suggested that this effect is the driving force for the growth of the cavity.
CHAPTER III

THE NATURE OF WATER IN EPOXY

As noted above we know that although hygrothermal effects and associated mechanisms of epoxy have for practical reasons been investigated for a long time [Loos 1981, DeNeve 1993, Imaz 1991, Brio 1993, Lee 1993, Adamson 1980, and Lucas 1989, 1993], the basic diffusion mode of water in epoxy resin are still not well understood. The issue to be addressed in this chapter concerns how water interacts with epoxy resins. Typical approaches that have been considered are as follows:

- Free volume approach, which presumes that water diffuses into epoxy resin and resides in free volume in the form of free water or clustered water. Chemical interaction between water molecule and epoxy resin is considered insignificant for this approach [Gupta 1985]. Water does not appear to be bound to polar groups in the resin or hydrogen bonding sites. There was only some clustering of water molecules in the polymer, rather than complete molecular separation [Woo 1987].
- Interaction concept, which suggests that water molecules couple strongly with certain hydrophilic groups such as hydroxyl or amine in epoxy resin [Moy 1980].
- Combination theory, which considers water molecules exist in epoxy in the form of both free water and bound state. Some water molecules form hydrogen bonding with

hydrophilic groups in epoxy resin while other water molecules are retained in free volume [Apicella 1985 and Adamson 1980].

The difference in interpretations of water sorption-effects is due in part to the reality that the hygrothermal environmental effects in epoxy are quite complex. The other reason is that most previous results used rather limiting testing and probing methods. Furthermore, systematic and integrated investigations have been lacking. Admittedly, there is some general agreement on some models, but, considerable disagreement still persists. There is no single theory with sufficient experimental support to account for all related phenomena. Sorbed water has significant influence on the mechanical performance of graphite/epoxy composites. Knowledge of the natural state of water molecules in epoxy resins is the most important and fundamental issue for the study of hygrothermal effects of epoxy resins and Gr/Ep composites. A review of previous literature suggests that a sophisticated approach and well designed experiments are necessary to gain knowledge and alley controversy. By investigating and understanding the nature of water in neat epoxy, it allows one to gain insight and results which can be applied subsequently to moisture sorption behavior in carbon/epoxy resin systems.

The aim of this chapter is to discern the nature and bonding characteristics of sorbed water in epoxy resins. An integrated experiment is designed and carried out by: a) investigating water absorption and desorption phenomena, and b) conducting nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) testing. Through this study a better understanding of the nature of water in epoxy resins is achieved.

3.1 EXPERIMENTAL

3.1.1 Materials

Three kinds of epoxy systems were used in this study. One is diglycidyl ether of bisphenol-A (DGEBA, Shell Epon828TM) and metaphenylene diamine (mDPA) epoxy system. The second is tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM, Ciba Geigy MY720TM) resin with 4,4'-diaminodiphenyl sulfone (DDS, DuPont) hardener. The third is ICI Fiberite 934TM epoxy resin which consists mainly of TGDDM resin, DDS hardener, with small amounts of other additives of which the types and their concentrations are proprietary. The chemical structures of these green materials are shown in Fig. 3.1. The three kinds of epoxies have been used extensively for high performance polymer matrix composites. The material preparation is described as follows.

DGEBA and 14.5 phr (part per hundred resin by weight) mPDA were heated separately to 75 °C in an oven until mPDA was melted. Then the epoxy resin and hardener were mixed thoroughly and degassed for 10 minutes. The degassed mixture was poured into a mold for curing. The curing procedure was 75 °C 2 h + 125 °C 2 h + 180 °C 8 h + 60 °C. Specimens were taken out of the oven after temperature ramped down to 60 °C. The temperature ramp rate was 1.5 °C/min..

TGDDM and 44 phr DDS were heated to 135 °C respectively, then, mixed and stirred until DDS was melted and a clear brown liquid was obtained. The material was degassed for 15 minutes. The curing procedure was: 135 °C (mixing and degassing) + 80 °C 1h + 100 °C 2 h + 150 °C 4 h + 200 °C 7 h + 60 °C and then the specimens were removed from oven. The temperature ramp rate was 1.5 °C/min.

The frozen Fiberite 934 epoxy resin was put in a mold and heated to 135 °C. The material was degassed for 10 minutes at 135 °C. The curing procedure was 135 °C 2 h + 177 °C 4 h + 190 °C 6 h + 60 °C and then the specimens were removed from oven. The temperature change rate was 1.5 °C/min.

$$CH_2 - CH - CH_2 - O - O - CH_2 - O - CH_2 - CH - CH_2 -$$

DGEBA









Fig. 3.1 Chemical structures of DGEBA, mPDA, TGDDM, and DDS.

After the three kinds of materials were prepared, Fourier transform infrared (FTIR) analysis was performed to determine the degree of cure. Epoxide groups have a strong IR absorption peak at 910 cm⁻¹. During the curing process, the intensity of the 910 cm⁻¹ diminishes gradually. When the epoxy resin is cured completely, all epoxide groups are opened and the 910 cm⁻¹ peak vanishes. If the material is not completely cured it has lower crosslinkage, mechanical properties, and T_g . During the hygrothermal exposure further crosslink may occur and it will influence the later experimental results



Fig. 3.2 FTIR spectrum of Fiberite 934 epoxy resin after being cured at 177 °C for 2 h. The existence of 910 cm⁻¹ means that the epoxy resin was not cured completely.



Fig. 3.3 FTIR spectrum of Fiberite 934 epoxy resin after being postcured at 190 °C for 7 h. The nonexistence of 910 cm⁻¹ means that the epoxy resin was cured completely.

significantly. Figure 3.2 shows the IR spectrum of Fiberite 934 epoxy resin after being cured at 177 °C for 2 h. The 910 cm⁻¹ peak has not vanished completely, which means the material is not fully-cured. Figure 3.3 shows the IR spectrum of Fiberite 934 epoxy resin after being postcured at 190 °C for 7 h. The 910 cm⁻¹ peak has vanished, which means the

material is fully cured. The other two epoxy resins showed similar curing characteristics at the 910 cm⁻¹ wavenumber. This test confirmed that all three epoxy resin systems were fully cured.

3.1.2 Water Absorption Test

3.1.2.1 Analysis

Consider a plate of thickness h exposed on two sides to the same environment. The plate is taken to be infinite in the y and z directions so that the moisture content inside the plate varies only in the x direction and the problem is one dimensional. Initially (time t = 0) the temperature, T_{i} , and the moisture concentration, c_{i} , inside the plate are uniform. The plate is suddenly exposed to a moisture environment in which the temperature, T_{a} , and moisture concentration, c_{a} , are constant. The objective is to determine the moisture distribution, c, and the total moisture content, m, of the material as a function of time. It has been observed that the diffusivity, D, changes very little with the moisture content [Augl 1975]. At a given temperature, the problem can be described by Fick's diffusion law [Shen 1981].

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$
(3.1)

 $c = c_i$ 0 < x < h $t \le 0$ (3.2a)

 $c = c_a$ x = 0; x = h t > 0 (3.2b)

Where c is the concentration of the moisture, t is the diffusion time, x is a dimensional coordinate, the thickness of sample is h, c_i is the moisture concentration inside the plate before the sample is exposed to a hygrothermal environment and it is uniform, c_a is the moisture concentration outside the plate after the sample is exposed to a hygrothermal

environment and it is a constant, and D is the diffusion coefficient (diffusivity), which is temperature dependent. The solution to Eq. 3.1 for the boundary conditions given in Eq. 3.2 was given by Jost [1960].

$$\frac{c-c_i}{c_m-c_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)} \sin \frac{(2j+1)\pi x}{h} \exp[-\frac{(2j+1)^2 \pi^2 Dt}{h^2}]$$
(3.3)

Here c_m is the maximum moisture concentration. The total weight of the sorbed moisture in the material is obtained by integrating Eq. 3.3 over the plate thickness.

$$m = s \int_{0}^{h} c \, dx \tag{3.4}$$

-

The result of this integration is:

$$G = \frac{m - m_i}{m_m - m_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp[-(2j+1)^2 \pi^2 {D_i \choose h^2}]}{(2j+1)^2}$$
(3.5)

m_i is the initial weight of the moisture in the material and mm is the weight of moisture in the material when the material is fully saturated, in equilibrium with its environment.

Experimentally, gravimetric analysis is used to determine the percent moisture content by moisture-induced weight gain of the material. Thus, in practice the parameter of interest is the percent moisture content defined as

 $M_t = 100 \text{ x}$ (weight of moist material - weight of dry material)/(weight of dry material)

$$= 100 x (W - W_d) / W_d \tag{3.6}$$

by noting that $W = W_d + m$ (3.7)

Where m is the weight of sorbed water in the material. Equation (3.5) may be rearranged in the form,

$$M_t = G(M_m - M_i) + M_i \tag{3.8}$$

Here M_t is the percent water gain with exposure time, M_m is the maximum water percentage, and M_i is initial water content. Equation 3.8 may be approximated by the expression for practically analytical use [Shen 1981]:

$$M_{t} = M_{m} \{1 - \exp[-7.3(\frac{Dt}{h^{2}})^{0.75}]\}$$
(3.9)

3.1.2.2 Test Procedures

In order to obtain the diffusion related parameters, such as diffusivity D, activation Q, and maximum moisture content M_m , following test procedures may be used to determine these parameters.

- 1. The test specimen is made in the form of a thin plate so that moisture enters predominantly through the surface of the plate.
- 2. The specimen is completely dried in a desiccator and its dry weight W_d is measured.
- 3. The specimen is placed in a constant temperature, constant moisture environment and its weight W is recorded as a function of time.
- 4. The moisture content (percent weight gain) $M_t = (W W_d)/W_d$ is plotted versus $t^{1/2}$, as illustrated in Figure 3.4.
- 5. The tests are repeated for a different exposure temperature.

The above procedure yields a series of curves similar in Fig. 3.4. Initially all curves are straight lines, the slope being proportional to the diffusivity of the material. After a long period of time the curves approach asymptotically the maximum moisture content M_m . The value of M_m is a constant and independent on temperatures when the material is fully submerged in water. The diffusivity is obtained from the initial slope of the M_m versus t^{1/2} curve [Shen 1981].

$$D = \frac{\pi}{16} \left(\frac{h}{M_{m}}\right)^{2} \left(\frac{M_{t2} - M_{t1}}{\sqrt{t_{2}} - \sqrt{t_{1}}}\right)^{2}$$
(3.10)

The activation energy Q and diffusion constant D_o can be obtained by plotting ln D(T) versus 1/T according to the following expression:

$$D = D_o \exp(-\frac{Q}{RT}) \tag{3.11}$$



Fig. 3.4 Illustration of the change of moisture content with the square root of time.

The three kinds of cured epoxy specimens were cut in dimension of 38 x 25.4 x 1.15 mm by a fine-grit diamond blade saw. The thickness of the samples is very small compared to the width and length, and the ratio of edge area and total surface area is $r \approx$ 5% so that edge effects could be ignored and the one-dimensional diffusion model as described above can be applied.

After conditioning at 110 °C for 24 hours to ensure that $M_i = 0$ and eliminate residual stress induced by material cutting, the specimens were placed into distilled water chambers with constant temperatures of 45, 60, 75, and 90 °C. The specimens were weighed periodically using an analytical balance with 0.01 mg resolution to determine the percent weight change, and, thus, water uptake. Each datum represents the average value of the three-specimen measurements. The water gain percentage was determined by Eq. 3.6. To ensure the removal of excessive surface (superficial) water, specimens were gently wiped dry using clean, lint-free paper towels.

After 1530 h exposure in a hygrothermal environment, samples were examined by environmental scanning electron microscopy (ESEM) to determine surface modification. Figure 3.5 shows ESEM micrographs of as-cured and water-saturated epoxy resins. Both show that there was no cracking or void formation on the resin surface after long term exposure.

3.1.3 Water Desorption Test

Subsequently, the water-saturated specimens were placed into a dry chamber with 0.3 L/min 100% dry air to desorb the water. The desorption process was conducted at 60 °C for 1450 h for all of the specimens. Then, the temperature was elevated to 140 °C for an additional 240 h desorption. The choice of using the two desorption temperatures emerged from the review of previous studies. The purpose is obtaining clear result and avoiding interference of two different bound states of water in the material. If the lower temperature is too low it takes long time for water desorption but if the temperature is too high it the material may be damaged but if



Fig. 3.5 ESEM micrographs of My 720 epoxy resin (a) as-cured and (b) hygrothermallyexposed at 90 °C for 1530 h. Both show that there is no cracking or void on the resin surface. temperature is too low the residual water could not be removed completely. The detail can be found in next section of this chapter. In desorption processing, specimens were also weighed periodically using an analytical balance to determine the percent weight change. Each datum is the average value of three samples.

3.1.4 NMR Test

NMR spectroscopy has been widely used in the investigation the behavior of water in epoxy resins since the mobility change of water molecule in epoxy can be determined by this spectroscopic method [Moy 1980, Jelinski 1985]. The chemical shift and width of NMR peak can reveal detailed information on the molecular mobility and interaction. NMR spectroscopy is a physical method for direct investigation of nuclear energy levels. The origin of these levels are related to the angular momentum **P** of the nucleus. Therefore, the NMR effect is based on a nuclear property. The majority of nuclei possesses an angular momentum, **P**, which is proportional to a quantity called spin, **I**.

$$\boldsymbol{P} = \boldsymbol{h} \boldsymbol{I} \tag{3.12}$$

The proportionality constant is Planck's constant h. Both P and I are quantum mechanical operators. The eigenvalue of I^2 is I(I+1), where I is spin quantum number which is integral and half-integral values. The angular momentum and thus the spin is proportional to the magnetic moment of the nucleus,

$$\boldsymbol{\mu} = \boldsymbol{\gamma} \boldsymbol{h} \boldsymbol{I} \tag{3.13}$$

where γ defines the magneto-gyric ratio.

If the nucleus is put in a magnetic field, the magnetic moment μ will have a different direction with the magnetic field due to interaction between magnetic moment

and magnetic field. From the point of view of quantum mechanics, the value of magnetic moment on the direction of magnetic field is

$$\mu_H = \gamma m h \tag{3.14}$$

where m is spin quantum number, m = I, I-1, I-2, -I+1, -I, total 2I + 1 values. For a nucleus, such as ¹H, with I = 1/2, magnetic moment μ has two directions in a magnetic field. The values of the magnetic moment on the direction of magnetic field is $\mu_{\rm H} = (+1/2)\gamma h$ and $\mu_{\rm H} = (-1/2)\gamma h$. According to electromagnetic theory, the potential energy due to magnetization, M, in a magnetic field, B_o, depends on the angle θ between the dipole moment and the field,

$$E = -MB_o = -MB_o \cos\theta = M_2B_o \tag{3.15}$$

where $M_z = |M|\cos\theta$ is the projection of the magnetization vector on to the direction of the magnetic field. The quantum mechanical operator corresponding to the energy is the Hamilton operator. The potential energy of a single magnetic moment in a magnetic field is given in analogy to the Eq. 3.15 by:

$$H_z = -\gamma h I_z \tag{3.16}$$

It is called Zeeman interaction. For this reason the lower index z is used. The energy levels E_m are defined as the eigenvalues of the Hamiltonian operator:

$$E_z = -\gamma hm B_o \tag{3.17}$$

Here m is the magnetic quantum number and its values are:

Thus a nuclear spin with quantum number I can be in one of 2I + 1 stable positions in a magnetic field. Nuclei like ¹H and ¹³C with spins I = 1/2 have two eigenvalues. These are referred to as spin-up and spin-down, depending on whether the z component of the

magnetic moment is parallel or antiparallel to the magnetic field (Fig. 3.6). The energy difference ΔE between neighboring energy levels is absorbed or emitted by a nuclear spin when it reorients and moves from one energy level to the next (Fig. 3.7). This energy difference determines the NMR frequency v_0 :

$$\Delta E = M_m - M_{m-1} / = \gamma h B_o = -h \omega_o = -h \nu_o \qquad (3.18)$$

It defines the position v_0 of the (Zeeman) signal in the NMR spectrum (Fig. 3.8). Once the frequency magnetic field equals to v_0 the nuclear magnetic resonance occurs. The observable NMR experiment is the frequency v_1 . Therefore data are generally given as the frequency shift related to a reference compound with σ_{ref} defining the origin of the σ scale. Chemical shift data δ are usually reported as the frequency shift from the reference compound giving a signal at $\sigma_{ref} = 0$ normalized by the resonance frequency of the reference compound in parts per million (ppm).

Relaxation is another important datum in NMR technique. It is the process by which the initial state of thermodynamic equilibrium is restored. There are two elementary kinds of relaxation. One is spin-lattice relaxation and the other is spin-spin relaxation. High mobility molecules have short relaxation time. Relaxation time has great influence on the width of NMR signal. According to Pauli Exclusion Principle:

$$\Delta E \Delta t \approx h \tag{3.19}$$

And we know
$$\Delta E = h \Delta v \tag{3.20}$$

SO

 $\Delta v = l / \Delta t \tag{3.21}$

This relationship tells us that the width of NMR signal is inversely proportion to relaxation time and molecular mobility.

Chemical shift, signal intensity, and signal width can provide important information regarding the molecular species, quantity, and mobility. It has been reported that cured epoxy resin, which has been soaked in water, exhibits in its broadline NMR spectrum a narrower peak due to absorbed water [Apicella 1983]. This peak, absent in a dry sample, has a width that is intermediate in magnitude between the broadline characteristic of protons in solid state and the quite narrow line arising from protons in



Fig, 3.6 Magnetic moment separation in a magnetic field B_o.



Fig. 3.7 Energy level separation of ${}^{1}H$ in a magnetic field B_{o} .



Fig. 3.8 Typical solid state NMR spectroscopy [Mehring 1983].

the liquid state. Since NMR line width decreases with increasing molecular mobility, the conclusion was drawn that the water molecules are in a state of intermediate mobility between that of free water on the one hand and molecules in the solid state on the other [Lawing 1981, Moy 1980].

Although many NMR reports have been published on sorbed water in epoxy resins, it is noted that there are no detailed NMR report on water in epoxy at different hygrothermal stages. In this study NMR was carried out to determine water/matrix bonding characteristics since the NMR peak width directly reflects molecular mobility and water/matrix interactions in the composites. Broader NMR peaks are indicative of tighter bonding and vice versa. A Varian VXR 400 solid state NMR spectroscopy operating at 400 MHz was used for ¹H testing. Resin was ground into small particles and the size was less than 1 mm. The spin speeds were 4000 and 6000 Hz.

3.1.5 DSC Test

The differential scanning calorimetry, or DSC as it is commonly called, is a thermal analysis technique which measures heat flow into or out of a material as a function of temperature. DSC is the most widely used of the commercially available thermal analysis technique, finding broad application in determining temperatures and heats of transformation. All materials, as they experience changes in temperature, undergo changes in their physical and/or chemical properties. These changes can be detected by suitable transducers which convert the changes into electrical signals which are collected and analyzed. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms formed in a constantan disk. As heat transferred though the disk, the differential heat flow to the sample and reference in monitored by area thermocouples. Although DSC can be used to evaluated a wide variety of different materials, such as oil, inorganics, pharmaceuticals, and foods/biological matter, its most prominent area of application is polymers. In polymers, there are six specific DSC measurements that are most frequently made. They are glass transition, crystallization, melting, crosslinking, oxidation, and thermally induced decomposition.

A TA Instruments 2920 modulated DSC with 2200 data acquisition and analysis system was used in this study to determine if water molecules resided in resin in a clustered state, since this has been a controversial issue has been proposed in previous study [Woo 1987]. The contention is that, if bulk or clustered water exists in water-saturated epoxy, when the sample is cooled slowly below 0 °C and then raised above 0 °C, a heat absorption peak corresponding to ice melting would be observed by DSC measurement. Water-saturated neat resin was sealed in aluminum pans and scanned over a temperature range from -30 to +50 °C. The temperature ramp rate was 5 °C /min with 50 ml N₂/min in the testing chamber.

3.2 RESULTS AND DISCUSSIONS

3.2.1 Water Absorption

The water sorption profiles of the three epoxy systems immersed in water at temperatures of 45, 60, 75, and 90 °C are shown in Figure 3.9. The profiles were plotted by water gain percentage vs. square root of time (hour). At the initial stage water gain is linearly proportioned to $t^{1/2}$. After immersion in distilled water for 1530 h, all specimens reached full saturation at these temperatures, 45, 60, 75, and 90 °C, respectively. The saturation water content (M_m) is similar for a given material irrespective of the immersion

temperature values. This behavior shows that the water diffusion behavior of the three materials is Fickian in nature. The Fiberite 934 and TGDDM+DDS systems have similar water gains of 6.95 and 6.80 wt% respectively because they have similar chemistry. The DGEBA+mPDA system has a much lower saturation level (3.35 w%) compared with Fiberite 934 and TGDDM+DDS systems. DGEBA+mPDA system did not show the two-step water absorption behavior reported by other researchers [Gupta 1985]. This difference may be due to different material preparation since they did not report the degree of curing of the material. After immersion in water for more than 400 h, the saturation levels for the three epoxies still showed a small increase. This increase may be associated with certain chemisorption of moisture during the hygrothermal process. Further discussion of this matter will be considered in the next section.

From absorption data, the diffusivity D was determined from the initial slope of the M versus $t^{1/2}$ curve (Eq. 3.10). The activation energy Q is obtained by plotting ln D(T) versus 1/T according to Eq. 3.11 (Figure 3.10). Here T is exposure temperature (°K). All of the diffusion-related parameters of the three epoxies are shown in Table 3.1.



Fig. 3.9 Water absorption profiles of the three epoxy systems at different temperatures exposed for 1530 h. The symbols are experimental data.



Fig. 3.10 Transverse diffusivity as a function of temperature to determine activation energy Q of the three epoxy systems.

Table 3	3.1 The d	iffusion-rela	ted parameter	s of the th	ree epoxy s	systems: (diffusivity I) at
	different	immersion	temperatures,	activation	energy Q,	and maxi	imum wate	r
	content	M _m .						

	$\frac{D_{45}}{\text{mm}^2 \text{ sec}^{-1}}$	$\frac{D_{60}}{\text{mm}^2 \text{ sec}^{-1}}$	D_{75} mm ² sec ⁻¹	D_{90} mm ² sec ⁻¹	Q Kcal/mol	Mm %
TGDDM + DDS	3.13x10 ⁻⁷	6.61x10 ⁻⁷	1.15x10 ⁻⁶	2.35x10 ⁻⁶	11.1	6.80
DGEBA + mPDA	3.35x10 ⁻⁷	7.93x10 ⁻⁷	1.35x10 ⁻⁶	3.14x10 ⁻⁶	12.2	3.35
Fiberite 934	2.08x10 ⁻⁷	5.03x10 ⁻⁷	8.96x10 ⁻⁷	1.34x10 ⁻⁶	10.4	6.95

3.2.2 Water Desorption

Water desorption profiles of the three epoxy systems resulting from baking in a dry-atmosphere chamber at 60 °C for 1450 h, then 140 °C for 240 h are shown in Fig. 3.11. The initial desorption rate of absorbed water is rapid. With time, the desorption process is slows down. Even though specimens were desorbed at 60 °C for 1450 hours, some water still remained in the specimens. The retained water could not be expediently removed at this temperature (60 °C) no matter how long the materials were baked. The trend of retained water is that the higher the immersion temperature, the more water is retained. The amounts of retained water of the three epoxy systems immersed in water at different temperatures for 1530h shows in Table 3.2. Subsequently, the specimens were baked at 140 °C for an additional 240 h to remove the retained water. This residual water phenomenon is not an entirely new one. Moy [1980], Marsh [1988], and Xiang [1993] found some absorbed water could not be removed unless a higher bake-out temperature was used.

Moy [1980] investigated epoxy-water interaction by DSC, infrared, NMR, and water absorption and desorption using TGDDM and DDS system. He found strong hysteresis of the desorption process leaving residual amounts of water that can only be removed by heating the polymer above 100 °C. This provided evidence for a strong epoxy-water interaction. Moy's water desorption result is shown in Fig. 3.12. Marsh [1988] and Springer reported their moisture solubility and diffusion results of epoxy-glass composite. They found some amounts of sorbed water could not be removed. They tried to remove the residual water at temperatures of 85, 100, 110 °C but the amount of retained water kept constant. Temperatures in excess of the glass transition temperature

(>120 °C) were required to remove the residual moisture (Fig. 3.13). They considered that the occupied bond sites set initially at the lamination were a significant factor in the absorption process. Xiang [1993] observed thermal spike effects on moisture absorption in epoxy/carbon fiber composite. The desorption curves revealed the presence of a residual weight increase which might arise in a small concentration of unremovable residual moisture, which increased with thermal spiking temperature (Fig 3.14). This behavior inferred that some water was in some way chemically reacted in the composite presumably with the matrix. Therefore the apparent residual moisture content could be in the form of either hydrolysis products or strongly hydrogen bonded water molecules.

Obviously 100-120 °C is a critical temperature range. In this study 60 and 140 °C desorption temperatures were selected. The consideration is based on 1) 60 °C is a relative low temperature which is high enough to remove ordinary (unbound) sorbed water will not remove residual (more strongly bound) water simultaneously, and 2) retained water can be removed at temperature of 140 °C without a significant influence on material's thermal stability. One can see from Table 3.2 that very small concentration of water in DGEBA + mPDA system could not be removed at this temperature.

It is quite evident that, based on our experimental water desorption results and the previous studies, there are two types of sorbed water, as characterized by bonding, in the hygrothermal process. One type is easily desorbed from the material and is classified as a physiosorbed water or ' Λ -bonded' water. In contrast, the other type of sorbed water is more difficult to remove by desorption and, thus is classified as a strong bonded water or ' Γ -bonded' water. Λ -bonded water is baked out in the first desorption stage. The additional 240 h



Fig. 3.11 Water desorption profiles of the three epoxy systems at 60 °C for 1450 h, then 140 °C 240 h. The symbols are experimental data and represent the samples with different bath temperatures in the water absorption process.

Table 3.2 The amount of retained water in the three water-saturated epoxies after desorption at 60 °C for 1450 h. The trend is that higher immersion temperature induces greater levels of retained water.

	Retained water of sample bathed at 45 °C then desorp. at 60 °C 1450 h (w%)	Retained water of sample bathed at 60 °C then desorp. at 60 °C 1450 h (w%)	Retained water of sample bathed at 75 °C then desorp. at 60 °C 1450 h (w%)	Retained water of sample bathed at 90 °C then desorp. at 60 °C 1450 h (w%)
TGDDM + DDS	0.29	0.32	0.34	0.44
DGEBA + mPDA	0.11	0.18	0.20	0.25
Fiberite 934	0.27	0.30	0.33	0.39



Exposure Time

Fig. 3.12 Moy's [1980] water desorption results.



Fig. 3.13 Marsh's [1988] water desorption results



Fig. 3.14 Xiang's [1993] water desorption results.

desorption at 140 °C is the second desorption stage associated with the desorption of Γ bonded water. From desorption data, previous studies have suggested the existence of the two different types of sorbed water but none persuades this matter with further as was done in the present study. This study shows a consistent evidence of two types of sorbed water. The rest of this chapter gives more evidence and discussion on this issue by further investigation on desorption behavior and NMR tests.

Table 3.3 and 3.4 show the desorption diffusivities of the three epoxy systems. Table 3.3 gives the desorption diffusivity of the three epoxy systems with 60 °C as the desorption temperature. The method to determine the diffusivities is the same as for absorption diffusivity (Eq. 3.10). The data indicate that the desorption diffusivity $(5 - 6 \times 10^{-6})$ 10⁻⁷ mm²/sec) is similar to absorption diffusivity at 60 °C temperature (5 - 7 x 10⁻⁷ mm^2 /sec). This suggests that the state of bound water desorbed at 60 °C is the same as that initially absorbed by the material. Table 3.4 is the diffusivity of the three epoxy systems at 140 °C desorption stage. There is no 140 °C absorption diffusivity for comparison. But we know that diffusivity depends greatly on temperature. Higher temperature results larger diffusivity. Extending the absorption diffusivity data, an extrapolative diffusivity at 140 °C is obtainable. Figure 3.15 shows this result and the value of diffusivity at 140 °C is in the order of 10⁻⁵ mm²/sec. Compared to the extrapolated data, the experimental desorption diffusivity is much lower $(10^{-6} - 10^{-7})$ mm²/sec) and even smaller than 90 °C absorption diffusivity. This result provides evidence that the retained Γ -bonded water has a much smaller degree of mobility than Λ -bonded water. That is, the bound state of Γ -bonded and Λ -bonded water is dissimilar.

Figure 3.16 shows that the amount of Γ -bonded water increased with exposure time while maintaining a fixed exposure temperature (90 °C). The amount of Γ -bonded water depends strongly on the exposure time and temperature. Both higher immersion temperatures and longer immersion times create more Γ -bonded water. Such behavior of the Γ -bonded water leads us to consider it as chemisorbed water because chemisorption processes depend strongly on exposure time and temperature [A. W. Adamson, 1990]. Marsh [1988] and Barrie [1984] also reported that the amount of Γ -bonded water depended on exposure time suggesting that longer the exposure time promoted more retained water. The small increase in the saturation level shown in Figure 3.9 may be associated with the increase of the retained water with exposure time.

	Sample immersed at 45 °C then desorbed at 60 °C $(mm^2 s^{-1})$	Sample immersed at 60 °C then desorbed at 60 °C (mm ² s ⁻¹)	Sample immersed at 75 °C then desorbed at 60 °C (mm ² s ⁻¹)	Sample immersed at 90 °C then desorbed at 60 °C (mm ² s ⁻¹)
TGDDM+DDS	6.43×10^{-7}	5.86 x 10 ⁻⁷	5.90 x 10 ⁻⁷	5.62 x 10 ⁻⁷
DGEBA+mPDA	6.22 x 10 ⁻⁷	6.27 x 10 ⁻⁷	6.33 x 10 ⁻⁷	5.99 x 10 ⁻⁷
Fiberite 934	5.55 x 10 ⁻⁷	5.66 x 10 ⁻⁷	5.67 x 10 ⁻⁷	5.40 x 10 ⁻⁷

Table 3.3 Desorption diffusivity of water in the material desorbed at 60 °C in a dry chamber.

	Sample immersed at 45 °C then desorbed at 140 °C $(mm^2 c^{-1})$	Sample immersed at 60 °C then desorbed at 140 °C (mm ² c ⁻¹)	Sample immersed at 75 °C then desorbed at 140 °C (mm ² c ⁻¹)	Sample immersed at 90 °C then desorbed at 140 °C (mm ² c ⁻¹)
TGDDM+DDS	1.39×10^{-6}	1.67×10^{-6}	2.27×10^{-6}	1.79 x 10 ⁻⁶
DGEBA+mPDA	1.61 x 10 ⁻⁷	6.86 x 10 ⁻⁷	9.77 x 10 ⁻⁷	2.01 x 10 ⁻⁷
Fiberite 934	1.45 x 10 ⁻⁶	2.35 x 10 ⁻⁶	2.94 x 10 ⁻⁶	3.06 x 10 ⁻⁶

Table 3.4 Desorption diffusivity of water in the material desorbed at 140 °C in a dry chamber.



Fig. 3.15 The extrapolated absorption diffusivity at temperature of 140 °C.



Fig. 3.16 The amount of chemisorbed water of the epoxy Fiberite 934 changes with immersion time at 90 °C.

3.2.3 Γ-bonded Water

To reveal the nature of the Γ -bonded water, a solid state NMR test for ¹H was carried out. After desorption at 60 °C for 1240 h, all Λ -bonded water was removed and Γ -bonded water was still retained in the epoxies. These samples are designated as semidried samples. Figure 3.17 shows ¹H NMR results of (a) dry and (b) semidried TGDDM+DDS samples. The broad peak of the dry sample means all hydrogen or hydroxyl groups in the material bond tightly with the bone structure. The spectrum of the semidried samples shows no difference with that of the dry epoxy even though Γ -bonded water is still in the materials. One might think that the NMR may not detect such a small amount (≈ 0.4 w%) of water due to the sensitivity limitation of the instrument. To prove that the NMR instrument is sensitive enough to detect such small amounts retained water,

0.3 w% water was added in a dry sample and tested its NMR spectroscopy. The result is shown in Fig. 3.17c. An extra peak can be seen clearly in this spectrum. As we know that the formation of Γ -bonded water needs much longer time. The new peak is associated with the Λ -bonded water. These results indicate that such a small amount of water is detectable by the instrument and can be clearly identified from its broad NMR background peak. The similarity of the dry and semidried spectra simply implies that Γ -bonded water bonds tightly with the epoxy network.

From the above experiments, it is concluded that Γ -bonded water is chemisorbed water in epoxy resins. Some investigators [Mijovic 1985] have insisted that the water can penetrate both the macrovoids and microvoids of the epoxies and stay there in physically bonded state. The water molecules in microvoids may be trapped and not easily removed. If there were only desorption results without other more detailed evidences, we would skeptically accept this idea. But we further consider the remaining water to be chemisorbed water not only because of the desorption behavior but also because of the desorption diffusivity, NMR experimental results, and the hygrothermal effects measurements discussed in Chapter 4 and Chapter 5. As a plasticizer, physiosorbed water decreases the glass transition temperature and degrades mechanical properties. The following two chapters will reveal that the Γ -bonded remained water contributes to the increase of the glass transition temperature and a slight enhancement in the mechanical strength. These results could not be explained by a simple model involving just physical trapping mechanisms.

Moy [1980], Bellenger [1989], and Apicella et al[1985] found that there was a strong interaction between water and specific functional groups such as hydroxyl and amine groups in the polymer resin. Γ -bonded water is representative of this portion of sorbed water. For a fully cured epoxy there are enough hydroxyl groups for forming bonds with sorbed water molecules. The existence of these large number of and strong polar groups makes epoxy resin be able to wet with variety of substances. Although this H₂O-OH bonding is not as strong as backbone carbon-carbon bonding (60 -100 Kcal/mol) [Atkins 1993], it is much higher than physical bonding energy of 0.5 - 2 kcal/mol (including Van der Waals bonding, dipole bonding, and interchain hydrogen bonding). Atkins [1990] reported that breaking hydrogen bonding of water requires energy of 2 - 20 kcal/mol [5 kcal/mol for water-water hydrogen bond].



Fig. 3.17 NMR spectra of ¹H for TGDDM+DDS system desorption at 60 °C for 1450 h. The results indicate that Γ-bonded water is tightly bonded with the epoxy network.

3.2.4 A-bonded Water

As we have seen in the previous section, Γ -bound state water has no influence on dry sample NMR spectrum. So any NMR spectrum change of water saturated epoxy comes from A-bonded water. This change comparing with dry sample presents the characteristics of A-bonded water. Three NMR spectra of the TGDDM+DDS epoxy system are shown in Figure 3.18: a) dry epoxy, b) water-saturated epoxy, and c) dry epoxy mixed with liquid water. The peak width of sorbed water is broader than that of liquid water and narrower than that of tightly bonded hydrogen and hydroxyl group in epoxy resin. The mobility of Λ -bonded water in epoxy is between free-water (liquid) and solid states. Jelinski et. al. [1985] investigated the nature of the epoxy-water molecule interaction using a quadruple echo deuterium NMR spectroscopy and revealed that water in epoxy resin is impeded in its movement. Antoon et. al. [1981] showed their FTIR results and proposed that the sorbed water was held by hydrogen bonding. The process of the A-bonded water diffusing into the resin matrix can be described as follows: the molecules of A-bonded water break the interchain bonds that exist initially in the epoxy resin and form weak hydrogen bonds via Van der Waals type of force. Figure 3.19 is the NMR spectra of Fiberite 934 and it shows how quickly the free (liquid) water is absorbed and changed into impeded A-bonded water. Figure 3.19-a is a spectrum of dry resin mixed with 1% liquid water. Liquid water and a small amount of A-bonded water can be seen clearly. Just ten minutes later, liquid water disappeared and all sorbed water molecules were impeded. This result showing quickly formation of Λ -bonded water again gives us a strong evidence that the Λ -bonded water is physiosorbed water.

Some studies suggested that there was some bulk dissolution or clustering of water in the epoxy [Woo 1987, Apicella 1985], whereas, others believed there was no free water in the epoxy [Moy 1980, Jelinski 1985]. To resolve this issue, a DSC test was conducted. The suggestion is that, if there is some bulk or clustering water in the epoxy, when the saturated epoxy is cooled below 0 °C for a while, then the temperature is elevated above 0 °C, there will be a DSC heat absorption peak corresponding to ice melting.



Fig. 3.18 NMR spectra of ¹H for TGDDM+DDS system. The results indicate that the mobility of Λ-bonded water in epoxy is between free-water and solid states.



Fig. 3.19 NMR spectra of Fiberite 934 show free (liquid) water changes into impeded Λ-bonded water with time. (a) dry resin mixed with 1% liquid water and tested.
Liquid water and Λ-bonded water can be seen clearly. (b) Ten minutes later, liquid water disappeared and all sorbed water molecules were impeded.

The samples were cooled to -30 °C and isolated for 5 min., then the temperature was increased with ramp rate of 5 °C/min. Water of 0.5, 1, 2, 5 w% was added to the dry epoxy samples and tested by DSC. Every sample has a DSC absorption peak at 0 °C,
which corresponding to ice melting. A calibration curve was obtained by measure the height of each absorption peak. The calibration curve is shown in Fig. 3.20. After calibration, the amount of free water in the water-saturated epoxies was determined. The DGEBA+mPDA system showed no free water for all samples with different immersion temperatures. For the TGDDM+DDS system, the 45 and 60 °C samples showed some free water (less than 0.4 w%) and the 75 and 90 °C samples showed no free water. Free water was found in all of the Fiberite 934 samples which were immersed at different temperatures. The DSC trace of the Fiberite 934 is given in Fig. 3.21. The amount of free water in Fiberite 934 epoxy after immersion in water for 2200 h is roughly determined by the height of endotherms and the results are shown in Fig. 3.22. The DSC testing results indicate that most of the physiosorbed water in epoxy is dispersed and only a very small amount (if any) of physiosorbed water is in free-water state. The reason Fiberite 934 samples show much more free water than the other two resins may be due to different additives in the resin.

The schematic drawing shown in Fig. 3.23 indicates the polymer network before and after water absorption. This schematic (Fig. 3.23) pictorially conceptualizes the bound states of water in epoxy resin based on the findings and interpretation of the study. The concept shows that before water absorption a huge number of interchain hydrogen bonds and a lot of hydrophilic hydroxyl groups exist in the material. After water saturation some water molecules break the interchain hydrogen bonds and form new Van der Waals type bonds with hydrogen. This portion of water is physiosorbed water. The effects of this interchain hydrogen bond break are plasticization and swelling. Some water molecules form tight bonds with polar hydroxyl groups and this portion of water is chemisorbed water. Some water molecules may stay in free water state and has no bound with epoxy network.



Fig. 3.20 The calibration curve of the amount of clustered (free-state) water in water saturated epoxy resin.



Fig. 3.21 DSC trace of water saturated Fiberite 934 resin for determining the amount of free water.



Fig. 3.22 DSC results of free water content in Fiberite 934 epoxy after immersion in distilled water at different temperatures for 2200 h. Bath temperature represents the samples' immersion temperatures in water absorption process.



Fig. 3.23 A schematic conceptualization of epoxy network and bonding characteristics before and after water absorption.

3.3 SUMMARY

Two types of bonded water are found in epoxy resins by water desorption measurement, desorption diffusivity calculation, residual water determination, time and temperature relations study of the retained water, and the NMR test on the resins at different hygrothermal stages. Depending on the water-resin bonding characteristics, they are designated as Λ -bonded water and Γ -bonded water. The Λ -bonded water is a physiosorbed water. The molecules of Λ -bonded water diffuse into the material and break the interchain hydrogen bonds that exist initially in epoxy resin and form weak hydrogen bonds via Van der Waals type force. Most of physiosorbed water is dispersed interchain hydrogen and only a very small amount of physiosorbed water is in free-water state. The Γ -bonded water is described as a chemisorbed water which interacts chemically with hydrophilic groups such as hydroxyl groups in the epoxies. The amount of Γ -bonded water depends strongly on immersion temperature and time. The relations of the two bonded water and the hygrothermal effects such as T_g and mechanical property variations in epoxy resins will be discussed in the next two chapters.

CHAPTER IV

T_g VARIATION OF EPOXY IN HYGROTHERMAL ENVIRONMENT

The glass transition temperature (T_g) is a very important material parameter for epoxy, epoxy matrix composites, and resin-based composites in general, because T_g determines the service temperature of the material. In most applications, epoxy is required to serve in a glassy state — below T_g . Also, T_g 's change after the material is exposed in a hygrothermal environment reflects the degree of plasticization of the material. It is well recognized that absorbed water has a significant influence on the T_g of epoxy. The water molecule in epoxy is a plasticizer.

A well-know method for predicting T_g of epoxy exposed to a hygrothermal environment is the so-called "polymer-diluent" model introduced by Kelley and Bueche [Kelley 1960]. This model is based on the semiempirical work of Williams, Landel, and Ferry [Williams 1955]. Kelley assumed that the diffusing media in polymers does not enter the original free volume and just stays in the extra free volume created by diffused media. McKague [1978] was somewhat indifferent to Kelley's assumption and introduced a modified model using α_{ge} and α_{tw} instead of $\alpha_e = (\alpha_{te} - \alpha_{ge})$ and $\alpha_w = (\alpha_{tw} - \alpha_{gw})$, respectively. The results were believed to be more closely related to the true T_g value of the material. Although this model has been modified the fundamental concept is the same: T_g is simply the function of water content in the material. That is more sorbed water causes lower T_g . This model suggests that the value of T_g is independent in exposure temperature and time.

In recent years, studies have revealed that water absorption behaviors of epoxy cannot be described by simply using a free volume model [Moy 1980, Apicella 1984, Adamson 1980, Bellenger 1989, Lelinski 1985, Barrie 1984, DeIasi 1978]. DeIasi [1978] found water in epoxy had different bonding states. He suggested that water that disrupts the interchain hydrogen bond could depress T_g , whereas, water that forms cluster or hydroxyl-water type groupings has no measurable effect on T_g . Mijovic and Weinstein [Mijovic 1985] found that the depression of the glass transition temperature in a Gr/Ep composite after water absorption is strongly dependent on the temperature of the environment during water absorption. Our previous work indicated that some graphite/epoxy composites immersed in different temperatures show a very large T_g difference (>35 °C), although the water uptake (content) is the same as determined by moisture induced weight gain [Zhou 1994].

The technical literature of reported T_g results for a given epoxy exhibits a rather wide scatter band of data [DeNeve 1993, Wright 1981]. Often, the variation may be explained by different material preparation. But, from the above experimental data [DeIasi 1978, Mijovic 1985, Zhou 1994] and by results presented in Chapter 3, hygrothermal history (exposure time and temperature effect) is expected to contribute to the variation in T_g results. To investigate the variation of T_g in a hygrothermal environment, a comprehensive study was conducted. Three kinds of epoxy systems used in Chapter 3 were employed in this study. T_g was measured at different hygrothermal stages by thermomechanical analysis (TMA). The results and discussions give us a better understanding of the T_{a} variation of epoxy in hygrothermal environments.

4.1 MATERIALS AND EXPERIMENTAL

The glassy state of polymer is a supercooled liquid state. Glass transition is a second-order phase transition. Such phase changes are characterized by slope discontinuities in a volume-versus-temperature curve, or, more generally, by finite jumps in first derivatives of volume and entropy such as expansion coefficient, specific heat, and compressibility. The temperature at which such a jump occurs is designated as T_g . Generally, corresponding to these different physical responses, three methods are used to determine T_g . They are differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA).

The DSC test is based on the measurement of the specific heat change. The amount of testing sample is small and usually less than 20 mg. The problem in using this method to test a water-saturated epoxy sample is how to keep moisture in the material. Although the sample is sealed in a pan during DSC testing, some moisture can still evaporate since the material mass is small. Moreover, since the phase transition curve may not be sharp enough, in some circumstances, it is difficult to obtain a precise transition temperature.

In DMA testing, dynamic modulus is measured as a function of temperature. T_g can be determined by the intersection of the two tangential lines of the modulus vs. the temperature. To prevent water desorption from the sample during a dynamic test, the sample can be coated with silicon vacuum grease (Lee 1993) or aluminum foil

[Chateauminois 1995]. The disadvantage of the DMA method is the requirement of a larger sample (i.e. $40 \ge 5 \ge 2$ mm) and a relatively slow scanning temperature rate which may induce drying of the sample during the testing. Furthermore, the testing results may be dependent on the experimental condition, i.e. the temperature scanning rate and the strain frequency [Chateauminois 1995].

TMA tests the expansion change of a sample through the measurement of dimensional variation vs. temperature. T_g is determined by the intersection of the two tangential lines drawn along slope discontinuities of the dimensional change vs. the temperature profile. During the process of measurement, water desorption is unavoidable. But the temperature ramp is usually 10 to 20 °C/min., less sorbed water is lost compared with DSC and TMA measurements. The merits of the TMA test are quickness, a small sample (i.e. 5 x 5 mm) requirement, and high sensibility. Consequently, a precise T_g result can be conveniently obtained by TMA test. The detail of principle and the methodology of determining T_g by TMA were reported by Carter [1978] and McKague [1978]. In this study, all T_g results are determined by TMA test at 15 °C/min. DSC is employed to reconfirm some TMA results.

The materials used in this experiment are the same as that in Chapter 3. They are 1) tetraglycidyl-4, 4'-diaminodiphenyl methane (TGDDM, Ciba Geigy My720) resin with 4,4'-diaminodiphenyl sulfone (DDS, DuPont) hardener; 2) diglycidyl ether of bisphenol-A (DGEBA, Shell Epon828) and metaphenylene diamine (mPDA) epoxy system; and 3) Fiberite 934 epoxy system. The details of the material preparation process have been described in Chapter 3. Specimens (5 mm x 5 mm x 1.5 mm) for T_g determination were cut from the three kinds of epoxies which were exposed at different hygrothermal stages (water absorption and desorption, different exposure time and temperatures). A TA 930 thermomechanical analyzer (TMA) with 2200 data acquisition and analysis system was used to determine T_g . Relatively low contact loads (500 mg load) were used for the TMA analysis. The temperature ramp rate was 15 °C/min. A TA instruments 2920 modulated DSC with 2200 data acquisition and analysis system was used to test T_g and compare with TMA testing method and results. In DSC test samples were sealed in aluminum pans and the temperature ramp rate was 5 °C/min with 50 ml N₂ /min gas flow in the testing chamber.

4.2 RESULTS

4.2.1 T_g Change with Exposure Time

The T_g changes of the three epoxy resins with exposure time in the water absorption process are shown in Fig. 4.1 - 4.3. The materials were isothermally immersed in water at 90 °C for 1530 h. The results show clearly that T_g increases gradually after the samples saturated by water. During this test process temperature was fixed and the water content of each material kept approximately a constant (Fig. 3.9). The T_g variation is a pure time effect. After 45 h exposure in water at 90 °C TGDDM+DDS samples were saturated and the T_g Value was 121 °C. 1500 h later the T_g value increased to 132 °C. For DGEBA+mPDA system the change is from 113 to 124 °C. Fiberite 934 shows T_g variation from 113 to 126 °C. This T_g change with exposure time was also observed in the other lower exposure temperature process. Figure 4.4 shows the T_g change of the three epoxy resins with exposure time at 90 °C immersion temperature and Figure 4.5 shows the T_g change of the three epoxy resins with exposure time at 60 °C immersion temperature. The upper figure of each T_g change profile figure is the corresponding water absorption data of the three epoxies at the same immersion temperature. Both figures (Fig. 4.5 & 4.6) indicate clearly that T_g decreases sharply after immersion in water. The minimum value of T_g is obtained when epoxy resin just saturates. Then, T_g increases with exposure time while the water content of the epoxies remains constant. The T_g increase is about 15 °C after immersion in water for 1530 h.

A lower immersion temperature required a longer time to saturate and this prolongs the time necessary to reach the minimum T_g value for all materials. Samples with 90 °C immersion temperature have higher T_g than the 60 °C samples. The 90 °C samples' T_g profiles look like an entire shift up of the 60 °C samples' T_g profiles for all of the three epoxies. The range of T_g between the minimum value of the 60 °C sample and the maximum value of the 90 °C sample is as great as 35 °C, although they have the same water content M_m .



Fig. 4.1 T_g change of TGDDM+DDS with exposure time, the exposure temperature was 90 $^{\circ}$ C.



Fig. 4.3 T_g change of Fiberite 934 with exposure time, the exposure temperature was 90 °C.



Fig. 4.2 T_g change of DGEBA+mPDA with exposure time, the exposure temperature was 90 °C.



Fig. 4.4 T_g change with exposure time. Samples were immersed in water at 90 °C for 1530h. The upper figure is the corresponding water absorption profiles at the same temperature.



Fig. 4.5 T_g change with exposure time. Samples were immersed in water at 60 °C for 1530 h. The upper figure is the corresponding water absorption profiles at the same temperature.

4.2.2 T_g Change with Exposure Temperatures

After immersion in water for 1530 h, all materials reached same moisture saturation irrespective of the immersion temperatures ($M_{max} = 6.8$ wt% for TGDDM+DDS, $M_{max} = 3.35$ wt% for DGEBA+mPDA, and $M_{max} = 6.95$ wt% for Fiberite 934). T_g variation with immersion temperature was measured and the results are indicated in Fig. 4.6 - 4.8. The results all show the same trend. Samples exposed at higher immersion temperature have higher T_g. The variation is quite broad. For the 45 °C and 90 °C immersion samples, the range in T_g is 45 °C for TGDDM+DDS; 43 °C for DGEBA+mPDA; and 39 °C for Fiberite 934. The data for Fiberite 934 resin immersion at different temperatures are the same as that for the Fiberite 300/934 graphite/epoxy composite (Chapter 7).

DSC testing was conducted to compare these results with the TMA results,. Figure 4.9 shows T_g values of DGEBA+mPDA by TMA and DSC testing. The data were obtained using a TA 2200 data acquisition and analysis system. The T_g values obtained using DSC and TMA are clearly comparable. However, T_g is much easier to be determined by TMA trace since the dimensional change is quite large and the slope discontinuities are sharp. As mentioned the glass transition is a secondary order phase transition. In DSC testing a finite jump of specific heat is observed. This change is relatively small compared to dimensional change. Moreover, in water saturated sample this change may be interfered by a water evaporation endotherm. It is suggested that TMA testing to determine T_g is a better method for water-saturated epoxy. TMA testing is quicker, more convenient, and more precise.



Fig. 4.6 T_g change of TGDDM+DDS with bath temperatures after immersion in water for 1530 h.



Fig. 4.7 T_g change of DGEBA with bath temperatures after immersion in water for 1530 h.



Fig. 4.8 T_g change of Fiberite 934 with bath temperatures after immersion in water for 1530 h.



Fig. 4.9 T_g test results of DSC and TMA. The material is DGEBA + mPDA immersion in water for 1530 h at different temperatures.

4.2.3 T_g Change at Various Desorption Stages

After immersion in water for 1530 h, all water-saturated samples were placed in a 60 °C chamber with 0.3 L/min 100 % dry air to begin the water desorption process. Water desorption was allowed to take place over 1430 h. Although most of the sorbed water was removed at the 60 °C desorption temperature, some remained and could not be removed until the desorption temperature was raised to 140 °C (Chapter 3). The amount of retained water has been shown in Table 3.2. Table 4.1 contains T_g values obtained at various experimental stages of the moisture effects study: a) as-received dry, b) water-saturated, c) semidried, and d) re-dried. It is interesting to note that at the semidried condition T_g is nearly recovered despite a small amount of residual water remaining in the resins. Subsequently, the samples were baked at 140 °C for an additional 240 h and all sorbed water was removed completely.

	T _g of dry as- prepared sample (°C)	T _g of sample saturated at 90 °C 1530 h (°C)	T _g of sample desorbed at 60 °C for 1450 h* (°C)	T _g of sample desorbed at 60 °C 1450 h & then 140 °C 240 h** (°C)
TGDDM + DDS	251	134	250	251.5
DGEBA + mPDA	173	124	173	173
Fiberite 934	218	126.5	218	219

Table 4.1 T_g change of the three epoxies in different hygrothermal stages.

* Semidried desorption condition (60 °C/1450h)

****** Re-dried desorption condition (60 °C/1450h + 140 °C/240h)

4.3 DISCUSSION

The experimental results indicate that the T_g of a water-saturated epoxy depends strongly on exposure time and temperature. When the material first reaches saturation, the depression in T_g has the lowest value. With time, however, T_g increases gradually. Higher immersion temperature and longer time induce greater T_g . Notably, in this experiment all specimens of a given material which were immersed in different environmental chambers showed the same water content. In accordance with the free volume theory, which supposes that the T_g value is determined simply by the amount (weight fraction) water in the material. Pertaining to the free volume theory, all specimens, regardless of the exposure temperatures and time, would possess the same value of T_g . The difference between the experimental results and the free volume theory is evident.

According to free volume theory T_g value of water saturated epoxy T_{gwet} can be calculated by using the two equations below [Kelley 1960]:

$$T_{gwet} = \frac{\alpha_e V_e T_{ge} + \alpha_w (1 - V_e) T_{gw}}{\alpha_e V_e + \alpha_w (1 - V_e)}$$
(4.1)

$$V_{e} = \frac{1}{1 + 0.01 M_{m} (\rho_{e} / \rho_{w})}$$
(4.2)

Here, ρ_e = density of dry epoxy; M_{sn} = equilibrium water content; V_e = volume fraction of epoxy; α_{re} and α_{ge} are rubbery and glassy linear thermal expansion coefficient respectively determined by TMA dimensional change trace; epoxy volumetric expansion coefficient α_e = $3(\alpha_{re} - \alpha_{ge})$; T_g of water $T_{gw} = 4$ °C; water expansion coefficient $\alpha_w = 4 \times 10^{-3}$ /°C; and density of water $\rho_w = 1$ g/cm³ [Browning 1978].

All the experimental data are listed in Table 4.2. The calculated T_{gwet} of the three epoxies are shown in the last row of Table 4.2. The difference in calculated T_{gwet} which is

based on the "polymer-diluent" model and the experimental T_g is as large as 40 °C (Fig. 4.1 - 4.8). This model may be applicable for some polymers in which there are no strong polar groups such as hydroxyls, however, polymer-diluent model is invalid for predicting T_g of water saturated epoxy resin where a dual-mechanism behavior dominates.

Table 4.2 Experimental data of the three epoxies. T_g of dry epoxy T_{ge} ; density of epoxy ρ_e ; equilibrium water content M_m ; volume fraction of epoxy V_e ; rubbery and glassy thermal expansion coefficient α_{re} and α_{ge} ; epoxy volumetric expansion coefficient $\alpha_e = 3(\alpha_{re} - \alpha_{ge})$; and calculated T_g of water-saturated epoxy T_{gwet} .

	TGDDM + DDS	DGEBA + mPDA	Fiberite 934
T _g (°C) (dry, as prepared)	251	173	218
$\rho_{e} (g/cm^{3})$	1.26	1.19	1.28
M _m (%)	6.8	3.35	6.95
Ve	0.9211	0.9617	0.9183
α _{re} (cm/cm °C)	6.7 x 10 ⁻⁵	1.45 x 10 ⁻⁴	8.4 x 10 ⁻⁵
α _æ (cm/cm °C)	1.86 x 10 ⁻⁵	2.8 x 10 ⁻⁵	2.4 x 10 ⁻⁵
α _e (cm3/cm3 °C)	4.5 x 10 ⁻⁴	6.1 x 10 ⁻⁴	5.4 x 10 ⁻⁴
T _{gwet} (°C) (calculated)	144	120	133

Since the previous models do not provide a satisfactory explanation of T_g variations observed for hygrothermally exposed epoxy resins, a new interpretation is

proposed in the present study. The combination of the experimental T_g variation results implies that there are two types of bound water. The water molecules associated with Λ bonded water (physiosorbed water) diffuse into the material and break the interchain hydrogen bonds which exist initially in epoxy resin and form weak hydrogen bonds via Van der Waals force. The consequence of the interchain hydrogen bond breakage is the increase in chain mobility and the sharp decrease in T_g . As more water is absorbed more hydrogen bond breakage occurs resulting in a precipitous drop in T_g . Provided only the physiosorbed water existed in the resin materials of this study, T_g would have the same value for all hygrothermally-exposed samples. This implies that T_g , determined experimentally, will be unaffected by exposure temperature and exposure time duration. That T_g only depends weight fraction of water uptake and not on exposure history (exposure time and temperatures) suggests that water exists in a single bond state in the resin. Data from the current study refuse this.

The effects of chemisorbed water (Γ -bonded water) on the value of T_g is not so direct. We have found that (1) the amount of Γ -bonded water increases with immersion time (Fig. 3.16), and (2) for a fixed exposure time, higher immersion temperature creates more Γ -bonded water (Table 3.2). The observation that both T_g and Γ -bonded water increase with longer exposure time and higher temperature in the water absorption process indicates that " Γ -bonded water" plays an important role in T_g change. A plausible mechanism is that the Γ -bonded water forms a secondary crosslink with hydrophilic groups such as hydroxyl in an epoxy network [DeNeve 1993] and this crosslink density increase contributes to T_g increase. Hence, the experimental T_g value is influenced by a two-mechanisms process involving physiosorbed (Λ -bonded) water that decreases T_g via breakage of interchain hydrogen bonds and chemisorbed (Γ -bonded) water which increases T_g via formation of a secondary crosslink. The T_g variation can be described as follows. When the epoxy initially reaches saturation, T_g reaches its lowest value (Fig 4.4 and 4.5) since the partitioning of water in the material, at this instant, is such that the amount of Λ -bonded water is maximum and the amount of Γ -bonded water is minimum. With exposure time and temperatures more Γ -bonded water is formed. The Γ -bonded water creates greater secondary crosslink density and, thus, an increase in T_g.

After Λ -bonded water is removed in the desorption process, Γ -bonded water is still retained in the resin and the T_g is recovered completely. This phenomenon should not be explained as that the Γ -bonded water has no effect on T_g without the presence of Λ bonded water. After physiosorbed water is removed, interchain hydrogen bonds recover quickly and this recovery cause the reversion or restoration of T_g. A possible reason why one does not observe the T_g increasing caused by Λ -bonded water at semidried stage is that the secondary crosslink effect on T_g is relatively weak when all interchain hydrogen bonds are recovered. In some cases, T_g increase induced by Γ -bonded water at the semidried stage can be observed (Chapter 7) [Zhou 1994].

This interpretation can be applied on previous works efficiently. DeIasi [1978], Moy [1980], and DeNeve et. al. [1993] reported T_g test results for epoxy resin. Their experiments were carried out at constant temperature and different relative humidity. They found that T_g was lowered with water uptake in the material. The explanation is that since they tested the specimens with the same exposure temperature and time and different relative humidity, all of the specimens should have the same amount of Γ -bonded water because Γ -bonded water is controlled by exposure temperature and time. The only difference is the amount of physiosorbed water. Higher relative humidity creates conditions for more physiosorbed water in the resin and, thus, lower T_g .

4.4 SUMMARY

The variation of T_g of epoxy exposed to a hygrothermal environment can be summarized as follows: 1) the change in T_g does not simply depend on the sorbed water content in epoxy resin, 2) T_g depends on the hygrothermal history of the materials, and 3) for a given epoxy, longer immersion time and higher exposure temperature induce higher T_g . Both physiosorbed water and chemisorbed water have influence on T_g . The experimental T_g value represents the combined effect of the two mechanisms. Physiosorbed water causes a decrease in T_g via the breaking of original interchain hydrogen bonds and the increasing chain mobility of the epoxy. Chemisorbed water causes a T_g increase due to the possible formation of a secondary crosslinking with hydrophilic groups in the epoxy resins.

CHAPTER V

SWELLING AND MECHANICAL PROPERTY CHANGE OF NEAT EPOXY IN HYGROTHERMAL ENVIRONMENTS

In many industrial and commercial applications, the dimensional stability and mechanical property change of epoxy command considerable attention. This is particularly the case when neat resin is subjected to a hygrothermal environment which can cause the resin to swell and degrade the mechanical properties of the material. Most of the related studies have focused on water effects in Gr/Ep composites and fiber-resin interface [Biro 1993, Lee 1993, Lucas 1993, d'Aimeida 1991, Frassine 1994] and not on the neat resins. Since the effect of water absorption in epoxy-matrix composite is manifested by a decrease in the matrix-dominated properties, before a comprehensive study is conducted on Gr/Ep composites, it is necessary to characterize the swelling and mechanical property change that occur to neat epoxy in a hygrothermal environment.

Swelling defines dimensional change due to moisture absorption, independent of thermal expansion. Swelling occurs when interchain hydrogen bonds are disrupted by sorbed water causing the intersegmental hydrogen bond length to increase [Kwei 1966]. Previous investigations on resin swelling can be summarized mainly by two different approaches. One is suggested by Adamson [1980] who considered the swelling efficiency of sorbed water to be temperature and concentration dependent. Sorbed water molecules may either occupy free volume, causing no swelling, or may interrupt interchain hydrogen bonding to cause swelling. The other approach is suggested by Hahn [1976] and others. They found that the absorbed water produces relatively little swelling until a critical amount of water is absorbed, and then the resin sample volume increases proportionally to the additional water content.

A number of investigations have revealed that sorbed water in epoxy acts as a plasticizer [Imaz 1991, Biro 1993, Lucas 1993]. After exposure in a hygrothermal environment for a period of time, all mechanical properties, including modulus, strength, and failure strain, of epoxy resin are degraded. Usually, the mechanical property variations observed are dependent on water content and exposure temperature [Browning 1978, Shen 1977]. Data on swelling and mechanical degradation are obtained by placing material in different relative humidity (RH) environments long enough for the equilibrium moisture uptake to be reached. The general results are that more sorbed water and longer exposure time induce greater mechanical property degradation. Notably, there are few reports on mechanical property variation of the materials with the same moisture uptakes but exposed to different exposure temperatures. Similarly, there is no compelling report emphasizing mechanical property variations at different hygrothermal stages including water saturated and partially water saturated stages.

In this chapter, swelling and mechanical properties variations under the conditions of same water content and different exposure temperatures were thoroughly investigated. The purpose is 1) to investigate swelling behavior of epoxy samples that have same water content achieved via different exposure temperatures, 2) to show that if the two types of bonded water have different effects on the extent of swelling, and 3) to demonstrate how mechanical properties vary for materials at different hygrothermal stages (i.e. dry, saturated, semi-dried, and re-dried epoxy).

5.1 MATERIALS AND EXPERIMENTAL PROCEDURE

As in previous chapters, the three epoxy systems investigated were: TGDDM+DDS, DGEBA+mPDA, and Fiberite 934. Specimens used to assess dimensional change due to moisture induced swelling were fabricated to the dimension of $38 \times 25.4 \times 1.15$ mm. Tensile test samples with dimensions of $89 \times 12.7 \times 1.5$ mm were subsequently machined into a dogbone contoured shape with gauge length and width of 38 mm and 6.35 mm, respectively. Flexure test samples were cut in dimension of $63.5 \times 1.5 \text{ mm}$. The hygrothermal exposure is the same as described in Chapter 3.

The dimensional change of specimen length (38 mm dimension) were measured periodically using a micro-caliper with a 0.025 mm resolution, and, then, the percent dimensional change was determined. Each dimensional change result was an average of three samples. The measurement error is about 0.13% [(38.025-37.975)/38x100%]. Tensile and flexural testing was conducted on the samples that had been exposed for various periods of time at different temperatures. An Instron 4302 mechanical test machine was employed to conduct mechanical tests. For the tensile test, the crosshead speed was 0.5 mm/min. For the three-point bending flexure test, the crosshead speed was 1 mm/min and the span was 25.4 mm. Each mechanical test result was an average of five samples. The standard deviation was obtained directly from test report.

5.2 SWELLING

A schematic of the experimental absorption and desorption process is shown in Fig. 5.1 to help understanding the different hygrothermal states. The diagram shows the hygrothermal exposure process described in Chapter 3. Before the material is placed in an environmental chamber for water absorption, the sample is referred to as a dry sample. After the material is saturated by water, the sample is referred to as a saturated sample. By the end of physiosorbed water desorption process, physiosorbed water is baked out and only chemisorbed water is retained in the epoxy. This sample is referred to as a semi-dried sample. After 140 °C desorption, sorbed water is removed and the sample is referred to as a re-dried sample.



Fig. 5.1 Schematic of experimental water absorption and desorption process.

Dimensional changes of the three epoxy systems with immersion time and temperatures are shown in Fig. 5.2. The characteristics of swelling in water absorption process are: 1) swelling occurs from the beginning of the water absorption process, 2)



Fig. 5.2 Dimensional change with immersion time and temperatures.

swelling profile is similar with its corresponded water sorption profile (Fig. 3.9), and 3) for a given epoxy resin, specimens have similar maximum swelling regardless the exposure temperatures. After saturation, samples exposed at different temperatures have the same water uptake and the water induced dimensional change is the same. Hahn [Hahn 1976] showed that the absorbed water produces relatively little swelling until a critical amount of water is absorbed, and then the resin sample volume increases proportionally to the additional water content. Figure 5.3 shows an essentially linear relation of swelling and water gain. The result means that swelling is proportional to water gain.

Table 5.1 indicates the results of dimensional change in different hygrothermal stages for the epoxies that were immersed in water at 45 °C for absorption and then desorption at 60 °C and 140 °C. When material is water saturated swelling reaches the maximum value. On semi-dried stage the dimensional change percentage is not zero and on the re-dried stage the dimension is recovered. This result indicates that both Λ -bonded water and Γ -bonded water influence on the dimensional change. To reveal the degree of the influences of the two bonded water on swelling, every one percent physiosorbed water and chemisorbed water induced swelling percentage is calculated respectively. All original data and calculated dada are listed in Table 5.2. These data show the influence of the two bonded water affect swelling. It is quite evident that both types of bonded water affect swelling but physiosorbed water causes greater swelling and chemisorbed water has less effect on swelling.



Fig. 5.3 Dimensional change with sorbed water content.

Table 5.1 Dimensional change at different hygrothermal stages. The samples were immersed in 45 °C water chambers for water absorption. Water desorption was conducted at 60 °C for 1450 h and 140 °C for 240 h.

	swelling of dry sample (%)	swelling of saturated sample (%)	swelling of semidried sample (%)	swelling of redried sample (%)
TGDDM + DDS	0	1.829	0.044	0
DGEBA + mPDA	0	0.767	0.008	-0.013
Fiberite 934	0	1.928	0.041	0

Property	TGDDM/DDS	DGEBA/mPDA	Fiberite 934
Total sorbed water (w%)	6.8	3.35	6.95
Λ-bonded water (w%)	6.52	3.23	6.68
Γ-bonded water (w%)	0.28	0.12	0.27
Total swelling (%)	1.829	0.767	1.928
A-bonded water induced swelling (%)	1.785	0.744	1.887
Γ-bonded water induced swelling (%)	0.044	0.023	0.041
Ratio of Λ -bonded water induced swelling/ Λ -bonded water	0.374	0.23	0.282
Ratio of Γ -bonded water induced swelling/ Γ -bonded water	0.157	0.19	0.152

Table 5.2 The influences of Λ -bonded water and Γ -bonded water on swelling.

5. 3 MECHANICAL PROPERTY CHANGE

5.3.1 Mechanical Property Change in Water Saturation Stage

In this section we will describe mechanical property variation of water-saturated (with constant water content) epoxies with different exposure temperatures. Hygrothermal effects on tensile and flexural moduli are shown in Fig. 5.4. The moduli of Fiberite 934 decrease after immersion in water at different temperatures for 1530 h. For Fiberite 934 the tensile and flexural moduli of water saturated sample are about 15% and 17% lower than that of the dry sample respectively. Exposure temperature (range from 45 to 90 °C) shows no influence on the degradation. The DGEBA+mPDA system has much lower saturated water content (3.35%), and no notable modulus (both tensile and flexural) difference is observed between dry and saturated samples.
Both Fiberite 934 and DGEBA+mPDA exhibit tensile strength decrease, but Fiberite 934 shows a much greater decrease (Fig. 5.5). Before being exposed to a water environment, Fiberite 934 has higher tensile and flexural strength than that of DGEBA+mPDA. After saturation both tensile and flexural strength are lower than that of DGEBA+mPDA since Fiberite 934 has much higher water saturation value (more than two times). The decrease of tensile and flexural strength of Fiberite 934 is about 25 - 56% and 15 - 44% lower than that of the dry sample respectively. Notably, the degradation is temperature dependent. In the temperature range of 45 - 90 °C strength decreases with exposure temperature increase. Compared with the 45 °C sample, the strength of 90 °C sample is approximately one third lower. Moisture has little influence on DGEBA+mPDA flexural strength and the tensile strength shows 15 - 20% decrease.

The most significant hygrothermal effect for any kind of epoxy is the large decrease in failure strain (Fig. 5.6). The failure strain decrease is strongly exposure temperature dependent. The failure strain of 90 °C hygrothermally exposed Fiberite 934 and DGEBA+mPDA is less than half of the dry sample's value. As observed by ESEM (Chapter 3) there is no visible crack and void in the resins after hygrothermal exposure for 1530 h. A notable change for all samples during the water sorption process is discoloration. The as-prepared samples are light brown or light yellow. After long time exposure, the color of all samples became darker and darker gradually. Higher exposure temperature resulted in darker color. The 90 °C samples almost became black. This phenomenon may be explained by chain scission. DeNeve [1993] studied water absorption in epoxy resin (DGEBA+DDA) by mechanical and IR test. He found some IR peaks changed with hygrothermal exposure process. A plausible chain scission mechanism

was given in Fig. 5.7. Notably, the epoxy resin he used is different from this study. Browning [1978] investigated Gr/Ep composites (TGDDM+DDS matrix) in high humidity environments. He pointed out that chemical chain scission of any substantial magnitude can be eliminated but very localized chemical chain scission in such areas as crack tips cannot be ruled out. Also, during water desorption process the network collapse due to water removing can cause chain scission. Owing to the chain scission caused polymer network change the mechanical properties will have significant influence and the T_g value may also be influenced. But from this study the influence in T_g is limited because T_g can be recovered completely after the material is redried.

Some epoxy shows great water absorption ability such as 6.95 % for Fiberite 934 and some shows small water absorption ability such as 3.35% for DGEBA+mPDA. Hygrothermal effects on mechanical properties are quite different for different epoxies. Mechanical properties such as modulus, strength, and failure strain of epoxy that has high water absorption decrease significantly in a hygrothermal environment. In contrast, less influence on the mechanical properties can be found in the epoxy with low water absorption. Some high water absorption epoxy has higher strength in dry sample and shows lower strength than low water absorption epoxy after saturation. For the choice of material which serves in a high humidity or marine environment, the first consideration should not be the strength of a dry sample but its strength after water absorption.

5.3.2 Mechanical Property Change in Different Hygrothermal Stages

The mechanical property changes in different hygrothermal stages are shown in Tables 5.3 - 5.7. The three kinds of epoxy samples were placed in 90 °C water chamber for water absorption and then desorption at 60 and 140 °C in a 100 % dry chamber.



Fig. 5.4 Change of modulus at different bath temperatures.



Fig. 5.5 Change of strength at different bath temperatures.



Fig. 5.6 Change of fracture strain after saturation at different bath temperatures.



Fig 5.7 Explanation of a chain scission in TGDDM+DDA system [DeNeve 1993].

Saturated samples show lowest mechanical values in all hygrothermal stages. After desorption at 60 °C (the samples are called semi-dried) the modulus was recovered and shown to be even higher than that of dry samples (Table 5.3 and 5.4). This increase is quite evident in the DGEBA+mPDA system. The modulus was recovered completely after all sorbed water was baked out at elevated temperature (the samples are called redried). The effect of water on the modulus of epoxy resin is reversible.

Water saturated samples show lower tensile and flexural strength. After 60 °C desorption, the flexural strength recovers completely and the tensile strength shows partial strength recovery (Table 5.5 and 5.6). When all sorbed water is desorbed, tensile strength still cannot recover fully. The strength of the re-dried sample is slightly lower than that of semidried samples. The strength of semi-dried specimen is higher than that of redried specimen.

The greatest influence of sorbed water on epoxy is the decrease in failure strain (Table 5.7). After saturation the failure strain is less than half of the dry sample's failure strain. In semi-dried stage, the fracture strain shows partial recovery. For re-dried samples, the failure strain is about two-thirds of the dry sample for Fiberite 934 and TGDDM+DDS system and just half for the DGEBA+mPDA system, although it shows less water-induced degradation on modulus and flexure strength. The decrease is strongly temperature-dependent and irreversible. The permanent strength and failure strain degradation is considered to be due to chain scission in water environment exposure [DeNeve 1993].

	Tensile modulus of dry samples (MPa)	Tensile modulus of saturated samples (MPa)	Tensile modulus of semi-dried samples (MPa)	Tensile modulus of re-dried samples (MPa)
TGDDM + DDS	1885 ± 39	1759 ± 50	1969 ± 102	1867 ± 45
DGEBA + mPDA	1448 ± 90	1388 ± 59	1652 ± 15	1480 ± 45
Fiberite 934	1861 ± 43	1565 ± 23	1872 ± 108	2021 ± 97

Table 5.3 Tensile modulus change in different hygrothermal stages. Water absorption temperature of all samples was 90 °C.

Table 5.4 Flexure modulus change in different hygrothermal stages. Water absorption temperature of all samples was 90 °C.

	Flexure modulus of dry samples (MPa)	Flexure modulus of saturated samples (MPa)	Flexure modulus of semi-dried samples (MPa)	Flexure modulus of re-dried samples (MPa)
TGDDM + DDS	4096 ± 101	3350 ± 59	4097 ± 112	4145 ± 95
DGEBA + mPDA	2662 ± 99	2697 ± 97	3069 ± 98	3297 ± 64
Fiberite 934	4130 ± 125	3324 ± 66	4077 ± 146	4186 ± 100

	Tensile strength of dry samples (MPa)	Tensile strength of saturated samples (MPa)	Tensile strength of semi-dried samples (MPa)	Tensile strength of re-dried samples (MPa)
TGDDM + DDS	96.5 ± 5.4	47.6 ± 2.4	77.9 ± 9.7	73.8±6.1
DGEBA + mPDA	80 ± 6.9	55.9 ± 5.0	60 ± 3.5	57.3 ± 2.8
Fiberite 934	93.1 ± 8.1	38.6 ± 3.7	88.3 ± 16	80.0 ± 7.0

Table 5.5 Tensile strength change in different hygrothermal stages. Water absorption temperature of all samples was 90 °C.

Table 5.6 Flexure strength change in different hygrothermal stages. Water absorption temperature of all samples was 90 °C.

	Flexure strength of dry samples (MPa)	Flexure strength of saturated samples (MPa)	Flexure strength of semi-dried samples (MPa)	Flexure strength of re-dried samples (MPa)
TGDDM + DDS	117 ± 15	86.9 ± 6.3	157 ± 12.5	159 ± 8.6
DGEBA + mPDA	141 ± 8.5	139 ± 3.6	149 ± 5.9	88.3 ± 2.0
Fiberite 934	162 ± 14.8	90.3 ± 11.8	179 ± 26	138 ± 4.0

	Failure strain of dry samples (%)	Failure strain of saturated samples (%)	Failure strain of semi-dried samples (%)	Failure strain of re-dried samples (%)
TGDDM + DDS	6.1 ± 0.70	2.4 ± 0.13	5.0 ± 0.88	4.8 ± 0.50
DGEBA + mPDA	10.2 ± 2.1	5.2 ± 0.73	4.4 ± 0.50	5.0 ± 0.25
Fiberite 934	6.7 ± 0.94	2.6 ± 0.29	6.0 ± 1.30	4.9 ± 0.30

Table 5.7 Tensile failure strain in different hygrothermal stages. Water absorption temperature of all samples was 90 °C.

5.4 SUMMARY

Swelling in epoxy is basicly proportional to water gain. Experimental results show that both physiosorbed water and chemisorbed water have influence on swelling. But effect of chemisorbed water is smaller than that of physiosorbed water.

Some epoxy shows large water absorption ability and some shows lower water absorption ability. Water environmental effects are quite different for these different epoxies. Epoxy with large water absorption ability exhibits a significant decrease of both modulus and strength when epoxy is water-saturated. Low water absorption epoxy shows no significant modulus change with a slight decrease of strength. The most significant hygrothermal effect for all kinds of epoxy is the large decrease of failure strain, a change that is irreversible. Also, the failure strain decrease is exposure temperature dependent. The cause may be due to chain scission during the hygrothermal process. In choosing an epoxy that serves in high humidity or in a marine environment, the primary consideration should be the nature of water absorption.

CHAPTER VI

DIFFUSION OF WATER IN GRAPHITE/EPOXY COMPOSITES

The results of hygrothermal effects in neat epoxy resins have been shown in previous chapters. In this chapter the behavior of water in Gr/Ep composites is investigated. The environmental effect of moisture on polymer matrix composites (PMCs) is of significant interest, particularly since mechanical and physical property modifications are generally manifestations of its presence. Many investigations regarding moisture diffusion in PMCs have been conducted [Blikstad 1986, 1988, Avaen 1988, Morii 1993, Whitney 1978, Loos 1981, Bonniau 1984, Shirrell 1978, Imaz 1991, Lucas 1993] that address various aspects of moisture-induced behavior. The non-Fickian diffusion behavior of moisture has been reported in PMCs by numerous investigators [Whitney 1978, Loos 1981, Bonniau 1978, Imaz 1991, Lucas 1993, Springer 1981]. The experimentally determined profile of moisture gained versus exposure time often deviated (higher or lower) from the theoretical Fickian curve.

Some diffusion profiles indicate a continuous gradual increase in weight gain, never attaining equilibrium [Grayson 1985]. Some profiles do not directly reach an equilibrium water content M_m and its profile is like a stair-shaped curve, which is called two-stage diffusion [Gupta 1985]. These phenomena were usually considered as that the epoxy undergoes a slow relaxation whose rate is much less than that of diffusion. But other research showed that it is because of the cracking developed in hygrothermal exposure [Browning 1978, Loos 1981]. Weight loss has been observed frequently. Researchers believe that it is attributable to irreversible chemical or physical break-down of a material. Most commonly, weight loss occurs in conjunction with hydrolysis, or the separation of a side group from the polymeric chain, or the dissociation of matter located at the vicinities of fiber/matrix interfaces. But direct evidence is lack. Many factors can influence material's diffusion behavior. The variation may be caused by material preparation, curing process, and non-stoichiometric ratio of resin/hardener. The question is that for a stoichiometric and completely cured epoxy system the diffusion behavior is Fickian or non-Fickian. If anomalous behavior is observed how to interpret it.

To better comprehend diffusion behavior in Gr/Ep, it is essential to pursue both extrinsic and intrinsic aspects of moisture-induced diffusion behavior. Earlier investigations measured the change in weight versus time experimentally to obtain the moisture diffusion profile, which was then compared to the theoretical Fickian diffusion curve. However, some studies did not give the original material preparation and some studies just used limited experimental methods to probe this complicate issue. No published work was found that deals extensively with weight change, dimensional change, and surface modification of Gr/Ep simultaneously. In this study, moisture absorption behavior in T300/934 Gr/Ep composite was investigated. Specimens were immersed in distilled water at 45, 60, 75, and 90 °C for more than 9000 hours. Weight gain and water-induced expansion were measured, while SEM microscopy was used to investigate the surface modifications. A crack/mass-loss model is presented which yielded a remarkably

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good description of the behavior of graphite/epoxy composites subjected to a water environment.

6.1 MATERIALS

The material used in this study was unidirectional T300/934 Gr/Ep composite laminate received from ICI Fiberite. The Fiberite 934 epoxy resin consists mainly of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) resin, 4,4'-diaminodiphenyl sulfone (DDS) hardener, with small amounts of other additives. The chemical structures of TGDDM and DDS are in Fig. 3.1.

The curing temperature of a T300/934 laminate is nominally 177 °C. The laminate layup consisted of 18 plies of unidirectional prepreg (O₁₈). They were pressed together in a vacuum bag using a cloth on the two outer surfaces that caused a resin-rich layer that had the appearance of a woven pattern. The fiber volume fraction was 66 percent as measured by the optical numeric volume fraction analysis (ONVFA) method developed by Waterbury and Drzal [1989]. The nominal axial, E_{11} , and transverse, E_{22} , moduli are 19 Msi and 1.5 Msi, respectively. Poisson's ratio, σ_{12} , is 0.28. Typical thermal expansion coefficient values, α_{11} and α_{22} , are -0.4 x 10⁻⁶ °C⁻¹ and 18 x 10⁻⁶ °C⁻¹. The matrix-dominated, transverse moisture expansion coefficient, β_{22} , is 20 x 10⁻² %M⁻¹, an order magnitude greater than β_{11} , the axial moisture expansion coefficient. The matrix resin of as-received composite was tested by FTIR. The result is in Fig. 6.1. The spectrum shows that the epoxy group characteristic peak 910 wavenumber is vanished and the material is fully cured.



Fig. 6.1 FTIR spectrum of the matrix resin of as-received Fiberite T300/934 composite. It shows that the material is fully cured.

6.2 EXPERIMENTAL

Specimens having the dimensions of 40 x 15 x 2.3 mm were cut from the laminate with a diamond saw. The edges of the specimens were subsequently ground using 600 grit abrasive paper to maintain consistently smooth edge surfaces. After conditioning at 80 °C for 6 hours to remove sorbed moisture on the surfaces and to eliminate residual stress caused by sample preparation, specimens were placed into distilled water chambers heated to constant temperatures of 45, 60, 75, and 90 °C. Specimens were weighed periodically. Once the specimens were taken out of the environmental chambers, the surface water was absorbed using a clean dry paper towel. Following the towel drying procedure, the specimens were left in room air for 15 minutes at room temperature before weighing. Then specimens were weighed by using an analytical balance with 0.01 mg resolution, and the percent weight change was determined. Compared with the immersion time, the weighing time is very short, and, because, the water diffusivity in the material is small the weight loss during weight measurement is negligible. Water induced expansion and corresponding dimensional change were measured by a micrometer. Optical microscopy and scanning electron microscopy (SEM) were used to investigate surface modification associated with cracking, mass loss, and swelling.

6.3 RESULTS

In Fig. 6.2, the weight change profiles are demonstrated for graphite/epoxy material at different temperatures. For ease of comparison, both the experimental and the theoretical water absorption curves versus the square root of time are plotted on the same figure. Solid lines represent weight gain assuming Fickian diffusion. Symbols represent

experimental data. Each symbol represents the average of three measurements. Because the ratio of thickness/width of the thin plate specimen is << 1, calculations of diffusion parameters were performed using a one-dimensional approach without incurring significant error. Provided the initial temperature and internal moisture distribution of the material are uniform and the exposure temperatures are constant, the diffusivity can be

expressed as
$$D = \frac{\pi}{16} (\frac{h}{M_m})^2 (\frac{M_{t2} - M_{t1}}{\sqrt{t_2} - \sqrt{t_1}})^2$$
. M_m is the equilibrium amount of sorbed water

and h is the laminate thickness. The diffusivities of T300/934 composite are shown in Table 6.1.

As seen in Fig. 6.2 during the initial stage of moisture absorption, the experimental data match the theoretical profiles very closely for all exposure temperatures. With time, however, differences between the theoretical and the experimental data profiles are readily observed.

The experimental data of the lower temperature curves provide better agreement with the Fickian diffusion curves. The data for the specimen immersed in 45 °C distilled water essentially coincide with the theoretical curve over an extended time period. The data of 60 °C and 75 °C specimens is nearly coincident with Fickian diffusion curves as the theoretical saturation level is approached. However, beyond the theoretical saturation level, the experimental data diverge from the theoretical curves. The 90 °C specimen data diverge from Fickian behavior before reaching the saturation level, as the experimental weight change is greater than that of the theoretical values. After being immersed in water for 1300 hours (4.68 x 10^6 sec.), a reduction in the weight change of the 90 °C



Fig. 6.2 The weight change of T300/934 graphite/epoxy composite immersed in distilled water at different temperatures. Solid lines represent theoretical Fickian diffusion and the symbols are the experimental data at different exposure temperatures.

Table 6.1. The diffusivity of T300/934 graphite/epoxy composite materials.

Temperature (°C)	45	60	75	90
$D(m^2s^{-1})$	2.87 x 10 ⁻¹³	5.66 x 10 ⁻¹³	1.43 x 10 ⁻¹²	3.63 x 10 ⁻¹²

specimens was observed. Beyond 4700 hours $(1.7 \times 10^7 \text{ sec.})$, the weight change profile data are even lower than the theoretical saturation level. The contrast between the experimental data and the theoretical Fickian curves of Fig. 6.1 will be elaborated upon later in this study.

Dimensional changes were measured periodically on specimens immersed in water at 60, 75, and 90 °C. The dimension along the fiber direction exhibited extremely high stability as no detectable dimensional change could be measured. This environmental stability is due to the high strength and stiffness provided by the reinforcing carbon fibers in the fiber direction. Since the carbon fiber is virtually impervious to water absorption, the longitudinal fiber direction dimension is considered invariant. Figure 6.3 shows the width change of specimens at different temperatures versus exposure time. When the maximum solubility limit is reached, no further dimensional change (moisture-induced expansion) occurs. Figure 6.4 shows the thickness change of the specimens at 60, 75 and 90 °C. The 60 °C specimen reached a stabilized dimension after 1600 hours. The 75 °C specimen reached stability after 1100 hours; and, the 90 °C specimen reached its maximum thickness change at 900 hours. After 1100 hours, the thickness change curve of the 90 °C



Fig. 6.3 Width change of T300/934 graphite/epoxy composite immersed in distilled water at different temperatures.



Fig. 6.4 Thickness change of T300/934 graphite/epoxy composite immersed in distilled water at different temperatures.

Figure 6.5 shows optical micrographs of polished specimens at different environmental exposure conditions. Notably, the dry specimen does not have cracks, whereas the 75 °C and 90 °C specimens clearly exhibit multiple cracks after being immersed for 4300 hours. Cracks develop on the surface of specimens that contact the water. Moreover, the crack depth increases with time. At 4300 hours, the average crack depth emanating from the surface into the laminate is about 0.5 mm. Some 90 °C specimens were sectioned along the centerline after immersion in water for 4300 hours. Light-optics micrographs revealed that cracks were not present on the newly polished centerline surface section. This is in contrast to numerous cracks that are associated with the old exterior surface. Subsequently, the laminate was immersed in water for 168 hours and many cracks developed on the newly polished surface. This experiment indicated that edge cracking near the surface is promoted when the surface is in contact with the water. Moreover, the extent of internal cracking is significantly less.

Figures 6.6 and 6.7 are SEM micrographs of the laminate surfaces at various test conditions. The surface layer is primarily neat resin (approximately 15 μ m thick). The woven-like surface pattern is due to the impression of the cloth on resin during the manufacturing process. Surface resin peeling of the laminate can be seen clearly (Fig. 6.7a) for the 90 °C test condition after 4300 hours immersed in water. The thickness of the resin-rich surface layer becomes thinner and smoother (Fig. 6.7b). This resin loss explains why the thickness dimension of 90 °C specimens exhibited a significant downward trend with exposure time.

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Fig. 6.5 Optical micrographs of T300/934 Gr/Ep composite before and after immersion in water for 4300 hours. a) dry specimen, no crack can be seen, b) 75 °C, and c) 90 °C specimens. Both of the 75 and 90 °C specimens have visible cracks.



Fig. 6.6 SEM micrographs for surface images of dry and 90°C specimens. The surface layer is primarily neat resin. The woven-like surface pattern is due to the impression of the cloth texture on epoxy resin from the manufacture process. a) dry specimen, no damage on the surface and b) 90°C specimen, there is resin peeling after 4300 hours immersion in distilled water.



Fig. 6.7 SEM micrographs of the surface of 90°C specimen after 4300 hours immersion in water. a) resin peeling is highly visible, b) peeling, cracks and dissolution.

6.4.1 Moisture-Induced Material Response

The hygrothermal environmental effects and behavior of PMCs are quite complex and controversy still remains. Rao and his coworkers consider that moisture absorption in permeable fiber/polymer composites can be characterized using a Fickian diffusion model [Rao 1984]. Lee and Peppas [Lee 1993] studied water transport in Gr/Ep composites. They observed that water absorption kinetics of the TGDDM resin-based composites could be modeled by Fick's law. But the DGEBA-based samples indicated non-Fickian behavior because internal cracks were found after immersion in water at higher temperatures (@ 90 and 100 °C) [Lee 1993]. Imaz et. al. found that the moisture absorption of Gr/Ep composites was Fickian but at higher temperature there is a slight tendency to increase saturation level. This trend was attributed to a slight irreversible degradation in the material [Imaz 1991]. Loos and Springer investigated the moisture absorption behavior of many kinds of resin matrix composites. Their [Loos 1981] results show that materials obey Fickian diffusion behavior at lower temperatures and non-Fickian behavior at higher temperatures. The most plausible explanation is that under a moist high temperature environment, microcracks develop on the surface and inside the materials. As the cracks developed, material was actually lost, most likely in the form of resin particles. As long as the moisture gain was greater than the material loss, the weight of the specimen increased [Loos 1981]. Shirrell [1979] also observed similar kinds of moisture-induced surface modification. Research by Bonniau et. al. confirmed the surface mass loss and dissolution [Bonniau 1984]. Weitsman et. al. [1993] theoretically calculated the non-Fickian moisture absorption profile and found that moisture uptake was 25% higher. In

their calculation [Weitsman 1993] residual hygrothermal stress significantly influenced non-Fickian behavior. In the present study, cracks, peeling, voids and surface dissolution of the Gr/Ep composite laminate were quite evident after long-time immersion in distilled water.

From the previous works cracking and mass-loss have been observed, but there is no systematic study and sufficient proof to discuss this problem. In this study water absorption, dimensional change, and surface modification were investigated. Both Fickian and non-Fickian diffusion were observed. Exposure temperature plays a key roll for the diffusion behavior of water in Gr/Ep composites. It is seen clearly that in the material response to the overall moisture absorption process, cracks (including surface voids) and the surface mass loss (including surface peeling and dissolving) has great influence on the apparent weight change behavior. Surface peeling and resin dissolution contribute to weight loss (a net decrease of the overall weight) of the specimen, whereas surface crack and voids between fibers trap water thus promoting weight increase. The apparent weight change profile encompasses the combined competing effects of water diffusion, physioadsorption of water at crack tips which promote weight gain in the laminate, and surface mass loss mechanisms which contribute to gross weight reduction. The formation of cracking is considered due to the large difference in water-induced stress between the fiber and matrix phase. Graphite fiber is water impermeable. During hygrothermal exposure there is no water-induced swelling in the fiber. Owing to the great difference in moistureinduced expansion, sheer stress develops along the graphite fiber and matrix interface. In the interior of the specimen, the stress equilibrium is maintained. However, at the

exterior, the stress equilibrium does not exist any more. When the sheer stress exceeds the adhesive fiber-matrix bonding strength, cracks may develop.

It must be noted that incompletely cured and non-stoichiometric material should not be included in this discussion. Correctly stoichiometric ratio of resin and hardener and properly curing process are of the critical factors. Non-stoichiometric material contains some uncrosslinked monomers. During long time hygrothermal exposure these monomer is easy to leach out and results water gain profile downward. If the curing process is uncompleted, even though the resin/hardener ratio is stoichiometric, low molecular weight oligmers exist in the material. Under hygrothermal conditions these relative small molecules are easy for leaching and hydrolysis resulted the diffusion curve going down. Incompletely cured epoxy has other significant influence on diffusion profiles. Further curing may occur in hygrothermally exposure process. This crosslinking results larger free volume and, then, more water diffuses into the material. Persistently increasing profiles are observed. Additives are another factor to influence the diffusion behavior. Additives are used to improve the mechanical property of the material to meet some specific requirement or improve manufacturing process. They are usually catalyst, accelerator, and flexor. The leaching of these additives makes apparent water gain decrease too. Some may have chemical reaction with water and much more complete phenomena will be observed.

6.4.2 Crack/Mass-Loss Model

Based on the experimental results a crack/mass-loss model has been developed. This model can be used to describe the water sorption phenomena of graphite/epoxy composite materials immersed in water at different temperatures. For the 90 °C specimen, classical diffusion processes are dominant and Fickian law is obeyed for the first 170 hours. Subsequently, cracking occurs by the mechanism described earlier. Owing to the trapped water at the crack tip, the sorbed water content increases. Therefore the weight change profile is higher than the Fickian curve for a certain period of time. After 1300 hours, a different dimensional change behavior takes place. The width dimension remains invariant after that period of time, but the thickness exhibits quite different behavior and is coincident with the weight change profile. SEM examinations indicate surface peeling and dissolution of the matrix phase with exposure time immersed in water. The contrast in behavior exhibited between the width and thickness of 90 °C specimen is due to different surface characteristics. A fiber-epoxy network exists on the width surface, and the fibers can hold and interlock the epoxy to prevent peeling. However, on the thickness dimension, a layer of neat epoxy resin exists (15 µm thick) on the surface with no interlocking by fibers (Fig. 6.8). At 90 °C the neat resin layer peels and dissolves away with time, resulting in a decrease of the gross weight of the specimen. When mass loss becomes the controlling mechanism, an overall weight reduction in the specimen is observed. This severe cracking and surface peeling did not observed for 90 °C neat resin since there is no fiber/resin interface. The great sheer stress due to the existence of the interface is the cause of cracking and peeling. Surface hydrolysis is observed for the neat resin but the degree is not as large as Gr/Ep composite because the exposure time is quite

different (9000 h for Gr/Ep and 1530 for neat resin). For the 75 °C specimens, at times less than 800 hours, no cracks develop in the



Fig. 6.8 Schematic diagram of unidirectional Gr/Ep composite prepreg.

specimen and only Fickian diffusion exists. After 800 hours, cracks develop and the water content increases. There is no or, at best, very limited surface mass loss so the water content gained due to cracks is maintained. The behavior of the 60 °C specimens is similar to that of the 75 °C specimens. The main difference is that cracks appear at a much later time and the crack density is much lower. No crack development or surface mass loss occurs on 45 °C specimens, so its water absorption behavior/diffusion is completely

Fickian. Aspects of non-Fickian diffusion behavior for the graphite/epoxy material in this study is clearly depicted in Figure 6.9. The solid lines in Fig. 6.9



Fig. 6.9 Moisture absorption profiles of a graphite/epoxy laminate showing experimental data and theoretical prediction of Fickian diffusion.



Fig. 6.10 The schematic diagram of typical weight change profiles of Gr/Ep composites in water environment.

represent the theoretical Fickian diffusion. The symbols represent experimental data. In stage I, moisture diffusion is characteristic of Fickian behavior. Stage II indicates non-Fickian behavior associated with microcrack formation, particularly at the free edge of the

test material. In stage III, the non-Fickian behavior is characterized by gradual weight loss of the specimen resulting from resin leaching and dissolution.

This crack/mass-loss model can also explain the previous moisture absorption research results not only for distilled water, but also for moist air, salt water, fuel, and other liquids if cracking and/or surface modifications are involved in the weight change process. In general, a hygrothermal environment influences the absorption behavior of graphite/epoxy PMCs and is a manifestation of the models demonstrated in Figure 6.10 which is a schematic depiction for typical weight change profiles of Gr/Ep composites in different hygrothermal conditions. If no cracking or mass loss occurs, then Fickian behavior is obeved as noted in Fig. 6.10a [Loos 1981, Imaz 1991, Rao 1984, Ghorbel 1993]. This situation generally occurs near the temperature region of T/Tg < 0.25, where T is the water bath temperature. In Fig. 6.10b, there is no cracking in the initial stage of moisture absorption in the material, and Fick's law is obeyed. Subsequently, cracking occurs and the experimental data deviate from Fickian behavior, resulting in increased water absorption [Loos 1981, Shirrell 1978, Imaz 1991]. In Fig. 6.10c, initially no cracks exist. Afterward, cracks develop, and then, dissolution and peeling of the resin occur [Lucas 1993]. There are two ways in which the profile of Fig. 6.10d is attainable [Loos 1981, Shirrell 1979, Lee 1992]. First, at the initial stage, there are no cracks or peeling although with time both mechanisms take place. Of these two competing mechanisms, mass loss due to surface resin peeling dominates the weight gain profile. Second, no cracks develop and the absorption curve obeys Fickian law until surface mass loss occurs. This situation can be found especially in neat resin. Figure 6.10e indicates that cracks develop quickly and, even in the linear absorption stage, the weight increase is higher than

that representing Fickian law behavior [Loos 1981, Shirrell 1978, Gupta 1985]. No mass loss is involved in the process. In the case of Fig. 6.10f, surface peeling is the dominant mechanism and the specimen rapidly loses weight [Loos 1981, Lee 1992]. The last two situations are most often observed at relatively higher temperatures (T/Tg > 0.5).

6.4 SUMMARY

Water sorption in a graphite/epoxy (T300/934) composite exhibited both Fickian and non-Fickian diffusion behavior. Diffusion data showed that time for the onset of non-Fickian behavior was inversely related to the exposure temperature. Anomalous (non-Fickian) behavior in the composite resulted from physical damage to the epoxy resin. Cracks, voids, and surface peeling were clearly observed by SEM and optical microscopy.

Moisture induced expansion of the T300/934 composite was measured in length (fiber direction), width, and thickness directions. Essentially no expansion due to water absorption was detected in the fiber direction dimension. Significant dimensional changes resulting from moisture-induced expansion were observed in the width and thickness directions of the laminate. The thickness decrease of the specimen at high temperature was associated with surface resin dissolution and peeling.

A crack/mass-loss model favorably describes the phenomenological behavior of Gr/Ep composite resulting from water absorption processes. At a low exposure temperature compared to Tg, there is no surface dissolution or physical damage of the material and the weight gain behavior is Fickian. With increasing exposure temperature, cracks, voids, surface peeling, and dissolution occur. Cracks can retain water which contribute to absorption behavior higher than the theoretical Fickian diffusion curve.

Surface peeling and dissolution contribute to reduction in the specimen weight and, consequently, the weight change profile data falls below the theoretical Fickian diffusion curve. The resultant weight change profile represents the combination of these two factors, cracking and mass loss. Depending on the mechanism that dominates the experimental data, either profile higher or lower than the theoretical Fickian curve is possible.

CHAPTER VII

HYGROTHERMAL EFFECTS ON GRAPHITE/EPOXY COMPOSITES

Having studied the diffusion behavior of water in Gr/Ep composites, we will discuss additional hygrothermal effects in this chapter. The hygrothermal effects have been extensively studied in Gr/Ep composites [Loos 1981, DeIasi 1978, Imaz 1991, Biro 1993, Lee 1993, Lucas 1993, Adamson 1980]. It is abundantly clear that hygrothermal condition degrades both the mechanical and physical properties of PMCs, particularly, epoxy-based composites. To date, however, due to the complexity of water interaction in epoxy resin and resin-fiber interface, there is not a single theory with sufficient experimental support, that explains the all hygrothermal phenomena in Gr/Ep composites. Also, the relationship between hygrothermal effects and the bonding characteristics of water molecules in epoxy matrix are still not fully understood.

The hygrothermal effects of absorbed water in epoxy systems are mainly plasticization (lowered T_g), mechanical degradation, and swelling. Investigations reveal that sorbed water in epoxy acts as a plasticizer [Shen 1981, Imaz 1991, Biro 1993, Lucas 1993, Wolff 1993]. Based on the free volume concept of polymeric materials, Kelley and Bueche [Kelley 1960] developed a polymer-dilute model to predict T_g variation. This is a classical method for predicting the variation of T_g in water-sorbed resin. Several investigators [Cairns 1984, Browning 1978] applied this model to epoxy resin/water

system and explained the dependence of T_g on water content. DeIasi [1978] suggested that water that disrupts the hydrogen bond to depress T_g , whereas, water that forms cluster or hydrogen-water type groupings has no measurable effect on T_g . Mijovic and Weinstein [1985] found that the depression of the glass transition temperature in a Gr/Ep composite after water absorption is strongly dependent on the temperature of the environment during water absorption. At the same absorbed water content, the T_g depression was greater at higher absorption temperature.

The mechanical effect of sorbed water in Gr/Ep composite is manifested by a reduction in elastic modulus and by a decrease in the matrix-dominated strength properties. Shen and Springer [Shen 1977] summarized the previous tensile modulus data of composites and concluded that for 0° and $\pi/4$ laminates, there appears to be very little change in the bulking muduli over the entire spectrum of water contents from dry to fully saturated in the temperature range of 200 to 450 K, whereas, for 90° laminates, the saturated moduli decreased considerably with increases in both the water content and temperature. Using the stress-strain data of various water-treated samples of neat resin and composites, Browning et al. [1978] conclude that, as water absorption increased and/or as temperature increased, the tensile modulus of the resin matrix and the transverse modulus of the composite decreased. Crossman et al. [1978] determined the tensile relaxation modulus after exposure to equilibrium moisture levels. They found drastic reductions in modulus and an enhanced rate of relaxation at higher temperatures and moisture contents.

Study of hygrothermal effects on Gr/Ep composite is more important than on neat epoxy because the final applications of epoxy as structure material are always in the form of Gr/Ep. The hygrothermal effects of neat epoxy have been investigated in Chapter 3 - 5. The questions in this chapter is 1) if there are two types of bonded water in Gr/Ep composites, 2) if T_g changes with hygrothermal history, and 3) if swelling and mechanical change mainly depend on physiosorbed water. All these questions will be answered in this chapter.

The aim of this study is to discern sorbed water induced hygrothermal effects in Gr/Ep composites by evaluation of: a) water absorption and desorption phenomena, b) dimensional changes, c) T_g modifications, and d) mechanical properties variations. By using these integrated experimental approaches, a more comprehensive understanding emerges regarding the hygrothermal effects in epoxy-matrix composites.

7.1 EXPERIMENTAL

7.1.1 Material

The material used in this study was unidirectional T300/934 Gr/Ep composite laminate received from ICI FiberiteTM. The Fiberite 934 epoxy consists mainly of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) resin, 4,4'-diaminodiphenyl sulfone (DDS) hardener. The chemical structures of TGDDM and DDS has been shown in Chapter 3. More detailed material information is included in Chapter 6.

7.1.2 Water Absorption and Desorption

Specimens with dimensions of $43 \times 15 \times 2$ mm were cut from the laminate panel using a diamond blade saw. The water absorption procedure is the same as the described in material section of Chapter 6. After immersion in distilled water for more than 9000 h, all specimens held at temperatures of 45, 60, 75, and 90 °C reached full saturation. To
conduct water desorption experiments, water-saturated specimens were placed into a heated chamber with slowly flowing dry air. Desorption was performed using a two-step process: (i) first, desorption took place at 60 °C for 1250 h followed by (ii) desorption at 100 °C for an additional 250 h. Each datum presented in the absorption and desorption profiles represents the average of weighing measurements of three specimens.

7.1.3 Glass Transition Temperature Tests

To determine T_g variations at different hygrothermal stages, a TA Instruments 930 thermomechanical analyzer with 2200 data acquisition and analysis system was used. The principle of T_g by TMA has been described in Chapter 4. Specimens (5 x 5 x 2 mm) for TMA measurement were cut from the hygrothermally exposed laminates at different absorption or desorption stages. To obtain more precise TMA data, the choice of the contact load value was motivated by the suggestion of Carter and his coworkers [1978]. Consequently, a 500 mg load was used for the TMA analysis. T_g values were determined by the intersection of two tangential lines of the TMA expansion curve below and above the glass transition regime [Carter 1978].

7.1.4 Infrared Tests

Infrared spectroscopy was used to determine the chemical change of the epoxy resin associated with bonding characteristics at various absorption and desorption stages. A Perkin-Elmer 1800 FTIR was used in this study. Resin powder was obtained directly from T300/934 composite by scraping with a sharp metal blade. In this study, 2 mg of epoxy powder was mixed with 200 mg of spectrum-pure grade KBr and pressed into thin, 10 mm diameter discs under a 5000 kg load. The spectral resolution was 4 cm⁻¹ and the final spectrum was averaged over 100 scans.

7.1.5 Mechanical Tests

Flexural testing was conducted on hygrothermally exposed composite laminate. An Instron 4302 mechanical test system was employed to conduct three point bending tests. The crosshead speed was 0.5 mm/min and the span was 25.4 mm. Flexural test specimens were smaller in size (43 x 7.5 x 2 mm) than those suggested by the standard test method ASTM D790-81. Double cantilever beam specimens (DCBs) were used to determine fracture energy results of Gr/Ep laminates. DCB tests were conducted in ambient room conditions (23 °C and RH 65%). To facilitate testing, aluminum hinges were adhesively bonded to the notched end of the DCB specimens. Testing was performed at a grip opening rate of 5.0×10^{-4} mm/s.

Fracture toughness, K_{tv} , was determined using a modified chevron notch short bar specimen as described by ASTM 1304. In this study, the K_{tv} fracture toughness test specimen is designated as the laminate short bar (LSB) specimen. A desirable, useful feature of the chevron-notch short bar test is simplicity. In stark contrast to other fracture toughness test methods, measurement of the fatigue precracking is not necessary. Furthermore, once the compliance calibration is determined for a specified specimen geometry, the fracture toughness values can be obtained independent of test material [Barker 1977, 1983]. Essentially, only the critical load is needed to determine the fracture toughness and the provided criteria for linear elastic fracture mechanics are satisfied. The short bar plane strain fracture toughness is determined by the expression, $K_{iv} =$ $A\beta(P_{crit}/B^{3/2})$, where A is a constant that depends on specimen dimensions and the elastic modulus, E. The parameter A is given as f(b,B, E), where b is the instantaneous crack front width, which widens with incremental crack advance, and B is the specimen width modulus, E. The parameter A is given as f(b,B, E), where b is the instantaneous crack front width, which widens with incremental crack advance, and B is the specimen width [Barker 1977]. P_{crit} is the critical load and β is a dimensional correction factor for slightly misdimensioned specimens. Testing was performed at room temperature in air. Tests were performed in displacement control on a Fractometer II short bar test system. The grip opening displacement rate was 5.8 x 10⁻⁴ mm/s. Sharp crack initiation is achieved under the influence of a high stress field occurring at the chevron notch tip. The sharp crack grows to a critical length in a stable manner. When P_{crit} occurs at the critical crack length, the fracture toughness can be determined.



Fig. 7.1 The laminate shot bar (LSB) test specimen.

7.2 RESULTS AND DISCUSSION

7.2.1 Water Absorption and Surface Modification

Water absorption and diffusion behavior in Gr/Ep composites have been investigated in Chapter 6. In this chapter, previous water sorption results are reiterated briefly and are intended to serve as background information for further discussion of the hygrothermal effects in Gr/Ep composites.

Examination of the water absorption profiles shows that, over a 45 - 90 °C exposure temperature range, both Fickian and non-Fickian diffusion behavior is exhibited (Fig. 6.1). Cracks, voids, and surface-resin peeling were observed (Fig. 6.4-6) by using optical and scanning electron microscopy (SEM). Anomalous (non-Fickian) moisture diffusion behavior resulted because of surface damage and physical modification of the epoxy resin. At low temperatures relative to T_g , no significant surface resin dissolution or physical damage to the material was observed, and, thus, the weight gained as a result of water uptake is characterized by classical Fickian diffusion. With increasing exposure temperature, however, cracks, voids, surface peeling, and surface dissolution occur. Microcracks retain water and consequently contribute to absorption profiles that deviate from the theoretical Fickian diffusion curves as noted by the solid-line profiles in Fig. 6.1. Material loss from the specimens by surface peeling, dissolution, and leaching contributed to weight reduction and, so, the weight change profile data fall below the theoretical Fickian diffusion curve. Consequently, the experimental weight change profile represents the combined influence of the two factors: (a) microcrack-induced excessive weight gain and (b) mitigated mass/loss-weight reduction. Depending on the dominant mass-change

mechanism, experimental data will exhibit either a higher or a lower water profile than the classical Fickian curve.

Some other important considerations are emphasized here. It is shown in Chapter 3 that for a given material, all hygrothermally exposed samples have the same water saturation level M_m . In other words, if Fickian diffusion is obeyed, the water content in the composite is the same irrespective of the bath (exposure) temperature. Second, cracks and other surface defects were observed for all hygrothermally exposed samples, except for the samples exposed at 45 °C. Therefore, water diffusion behavior in the composite at 45 °C is considered to be completely Fickian. Cracktips, microcracks, and surface defects trap water by surface tension and capillary phenomena. Such trapped water is not controlled by classical Fickian diffusion mechanisms. Such trapped water is classify as Θ -bonded water. Θ -bonded water contributes to excessive (non-Fickian) weight gain.

7.2.2 Water Desorption

Figure 7.2 shows water desorption profiles of 45, 60, and 75 °C for hygrothermally exposed specimens resulting from baking in a dry-atmosphere chamber at 60 °C for 1250 h and, then, at 100 °C for 250 h. The initial rapid desorption of water results from basic evaporative losses of surface trapped water (Θ -bonded water) at cracktips and other surface and near-surface defects. Once Θ -bonded water sources are exhausted, the water desorption rates for all (@ 45, 60, and 75 °C) specimens approach similar values.

After desorption at 60 °C for 1250 h., water, albeit a small amount, is still retained in the specimens. This retained water is not readily removed at this temperature (i.e. 60 °C) regardless of how long the desorption process continues. This phenomenon is the 144



Fig. 7.2 The weight change profiles of the T300/934 composite desorption at 60 °C for 1250 h and then at 100 °C for 250 h.

same as in epoxy resin reported in Chapter 3. The desorption profiles in Fig. 7.2 also indicate that composite specimens exposed at higher immersion temperatures retain more water in the resin matrix. To completely expel the retained water, baking at 100 °C for an additional 250 h was required. From the desorption results, it is clear that two types of sorbed water, like in neat epoxy resin, exist in the hygrothermally exposed Gr/Ep composites. One type is readily desorbed and is classified as "physiosorbed" water or Λ bonded water. In comparison, the other type of sorbed water is more difficult to bake out and is, thus, classified as strongly bonded water or chemisorbed Γ -bonded water. The Λ bonded water is baked out in the second desorption stage (Fig. 7.2). Γ -bonded water, however, can only be removed in the third desorption stage, which is associated with strong-coupled water molecules with matrix resin. Much more detailed information about the properties of the two bounding state of water can be found in Chapter 3.

We have classified the three types of bonded water involved in the hygrothermal process in Gr/Ep composites. In the following sections, the main hygrothermal effects of Gr/Ep composites and how the hygrothermal effects are influenced by the three types of sorbed water will be discussed.

7.2.3 Change of Glass Transition Temperature

The T_g for specimens conditioned at varying hygrothermal stages is shown in Figs. 7.3 - 7.6. The data of Figs. 7.3 - 7.6 indicate that: i) the T_g of all water saturated samples decreased dramatically compared to the dry specimen, ii) the saturated specimens hygrothermally exposed at low temperatures render lower T_g , iii) the T_g 's of redried specimens baked at 60 °C for 1250 h are slightly higher than the T_g of as-received,



Fig. 7.3 T_g of the four saturated specimens after immersion in water for more than 9000 h at different temperature.



Fig. 7.4 T_g of the four saturated specimens after desorption at 60 $^{\circ}$ C for 1250 h.



Fig. 7.5 T_g of the four saturated specimens after desorption at 60 $^{\circ}$ C for 1250 h and then at 100 $^{\circ}$ C for 250 h.



Fig. 7.6 The T_g variations with the different immersion temperatures and desorption stages.

dry material, and iv) T_g is fully recovered after desorption at 60 °C for 1250 h and then 100 °C for 250 h. The difference in T_g values between the saturated 45 and 90 °C samples is about 37 °C. These results strongly suggest that Λ -bonded water contributes to the reduction in T_g , whereas, Γ -bonded water does not contribute to the reduction of T_g . Moreover, Γ -bonded water enhanced T_g slightly.

DeIasi [1978], Moy [1980], and DeNeve [1993] reported on T_g test results for epoxy resin. Their experiments were carried out at constant temperature and different relative humidity. They found that T_g was lowered with increased water uptake in epoxy resin. Previous studies [DeIasi 1978, Moy 1980, DeNeve 1993] have shown that T_g and ΔT_g in Gr/Ep composites depend only on the "amount" of absorbed water [$T_g = f(\%M)$]. According to their results, one would expect that T_g values of the specimens in this study should be the same since the water contents of all the specimens are the same (1.2 w%). However, results of the present study suggest that T_g does not depend simply on the sorbed water content in the resin, but also on exposure (bath) temperature and time [$T_g = f$ (%M, T, t)].

From the discussion of section 7.2.1 we have revealed that, irrespective of the bath temperature, the sorbed water content of all hygrothermally exposed specimens reaches a similar saturation level. Furthermore, as exhibited in Fig. 7.2, the desorption profiles plateau at different water content levels depending on the hygrothermal exposure temperature. Specimens exposed at higher temperatures render correspondingly higher plateaus. Also, higher immersion temperatures promote Γ -bonded type water at the expense of Λ -bonded water. More Γ -bonded water and less Λ -bonded water resulted in apparently higher T_g's (Fig. 7.6).

The results of this study are consistent with previous investigations [DeIasi 1978, Moy 1980, DeNeve 1993]. As noted in earlier investigations [DeIasi 1978, Moy 1980, DeNeve 1993], specimens were tested at the same exposure temperature and time, but at different relative humidities. Regarding this hygrothermal history, all the specimens in these studies would possess the same amount of Γ -bonded water, since the amount of Γ bonded water is controlled by exposure temperature and time. The only difference exists in the amount of Λ -bonded water (physiosorbed water). Higher relative humidity imposes conditions for enhancement of physiosorbed water in the resin and, consequently, lower T_g 's. The T_g variation in Gr/Ep composites and neat epoxy resins is remarkably consistent after long time exposure in hygrothermal environments. The comparison results are given in Table 7.1.

Table 7.1 The comparison of the T_g results in the long time exposed epoxy Fiberite 934 and Gr/Ep composite Fiberite T300/934.

	Exposure at 45 °C	Exposure at 60 °C	Exposure at 75 °C	Exposure at 90 °C
T _g of Fiberite T300/934	89	102	119	126
T _g of Fiberite 934 resin	87	106	112	127

7.2.4 Mechanical Testing Results

Three-point bending tests were carried out on 90 °C specimens at various absorption and desorption stages. Table 7.2 shows the flexural testing results. The saturated specimens exhibited the lowest flexural strength. After desorption at 60 °C for 1250 h, the Λ -bonded water was removed and the flexural strength recovered to a strength level slight higher than that of the as-received dry specimen. It should be noted, however, that Γ -bonded water still remains in the resin matrix at this desorption stage. Enhanced desorption at 100 °C for 250 h removed all the Γ -bonded water and the flexural strength reverted to that of the as-received dry specimen.

Fracture energy results for the saturated Gr/Ep laminate are shown in Fig. 7.7. With the increase of immersion temperature, the fracture energy tended to increase. For the 90 °C specimen, the fracture energy was even higher than that of the dry specimen. Again, it is contended that higher immersion temperatures induce additional secondary crosslinking which contributes to a slight increase of the fracture energy. Also, enhanced fracture toughness is attributable to energy absorbing mechanisms such as matrix plasticization and fiber bridging.

Gr/Ep fracture toughness results determined using laminate short bar specimens (LSBs) are shown in Fig. 7.8. As indicated in Fig. 7.8, sorbed moisture degrades the delamination fracture toughness (DFT) in the composite. Significant degradation in delamination fracture toughness occurred with moisture sorption under severe hygrothermal conditions. The reduction in mode I delamination fracture toughness is approximately 60% following hygrothermal exposure of the Gr/Ep laminate for 1.3×10^7 s. It has been suggested that plasticization of the matrix can lead to an increase in delamination fracture toughness [Jordan 1987, Bradley 1985]. That the DFT should increase was attributed to the enhancement in the moisture-induced crack tip plastic zone size. The contention was that the increase in plastic zone size due to plasticization enhances plastic energy dissipation at the crack tip, thus, effectively increasing the fracture toughness of the laminate. The decrease in the laminate fracture toughness

Table 7.2. Three-point bending test results of the 90 °C samples at different hygrothermal stages.

	Dry specimen	90 °C 9000h	90 °C 9000h in	90 °C 9000h in water
	(as-received)	immersion in	water then desorb.	then desorb. at 60 °C
		water	at 60 °C 1250h	1250h and 100 250h
Max. stress (MPa)	626	496	703	642



Fig. 7.7 The fracture energy results of the T300/934 Gr/Ep composite saturated in water for different hygrothermal conditions.



Fig. 7.8 The effect of moisture sorption on delamination fracture toughness is exhibited for Gr/Ep composite laminates.

observed in this study with matrix plasticization (softening) is in contrast to the previously published results [Law 1984, Jordan 1987, Bradley 1985]. This dichotomy can be rationalized by the realization that there is a competing effect to ability of the plasticization to dissipate crack tip strain energy and, thus, enhance fracture toughness. This competing effect is the weakening of the bulk matrix and the fiber/matrix interface phase in the laminate due to matrix plasticization by sorbed moisture. Particularly, the contribution of fiber/matrix interfacial fracture to overall crack propagation and interfacial debonding in moisture-sorbed Gr/Ep laminates was rather extensive as noted in this investigation. Morgan [1980] and others [Lucas 1989, Garg 1985, Imaz 1991] have reported several degrading effects of moisture on physical and mechanical properties of thermoset resins. Among the effects noted is that moisture lowers the tensile strength, elongation and modulus of epoxy. Also, sorbed water tended to enhance the susceptibility of the matrix to cavitation and plastic flow process. Preferential cracking along the fiber/matrix interface is exhibited in Figs. 7.9 for a Gr/Ep laminate exposed to hygrothermal conditions. Examination of the crack tip region shows major cracking in the interfacial region and microcrack link up of the inter-matrix region with interfacial cracking. In addition to primary fracture along the interfacial region (interface phase) significant secondary cracking is observed. The secondary cracking is caused, presumably, by residual stresses in the matrix resin as a result of plasticization by moisture. The fracture characteristics of Fig. 7.9b are indicative of a weakened interface as the crack appears to meander from the top fiber to the lower one. Macrofractography reveals such cracking branching as hackles [Garg 1985, Morris 1977] due to tensile stress relief in matrix-rich side of the main crack faces.

7.2.5 Swelling and Dimensional Change

Table 7.3 shows the dimensional change of the 90 °C specimen at different absorption and desorption stages. At the saturation level, the dimensional change due to swelling reaches a maximum value. After desorption for 60 °C 1250 h, the dimensions of the specimens essentially recover to the as-received dry specimen dimensions even though Γ -bonded water still remains in the specimen at this stage. Adamson [1980] suggested that water molecules may either occupy free volume causing no swelling or interrupt interchain hydrogen bonding causing swelling. The results in Table 7.2 indicate that Λ bonded water contributes mainly to swelling, whereas, Γ -bonded water has no significant influence on swelling.



Fig. 7.9 Fracture in the crack tip region is shown for Gr/Ep composites. (a) Fracture occurs along the fiber matrix interface. (b) Fracture is shown at the interfacial regions between two fibers.

	Dry specimen (as- received)	90 °C 9000h immersion in water	90 °C 9000h in water then desorb. at 60 °C 1250h	90 °C 9000h in water then desorb. at 60 °C 1250h and 100 °C 250h
Width(mm)	43.484	43.881	43.503	43.471
% change	0	0.9	0.043	-0.029

Table 7.3. Dimensional change of the 90 °C samples at different hygrothermal stages.

7.2.6 Infrared Results

Although many [Moy 1980, Adamson 1980, DeNeve 1993] believe that water can interact with epoxy resin, there is little direct infrared evidence to verify this claim [DeNeve 1993, Antoon 1981]. In this study, FTIR spectroscopy was conducted, and results were obtained that allowed inferences to be made concerning matrix/water interactions. Fig. 7.10 shows the infrared spectra results of several temperature and moisture-conditioned specimens. Included in Fig. 7.10 are spectra of as-received dry, long-time baked dry, and water-saturated 934 epoxy resin specimens that were exposed to different water immersion temperatures. The basic chemical compounds of the Fiberite 934 are the resin, tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), and the hardener, 4,4'-diaminodiphenyl sulfone (DDS). There are other additives in the Fiberite 934 resin, but these chemical compounds and their concentrations are proprietary. For this reason, it is difficult to ascertain in this study all the detail chemistry of the 934 resin from IR results. However, these results still reveal some useful information. The 1594

 cm^{-1} and 1512 cm^{-1} peaks represent carbon-carbon double bonding v(C=C) from the aromatic ring of TGDDM. The 1720 cm⁻¹ is thought to be derived from the vibration of carbon-oxygen double bonding v(C=O). However, we know there is no C=O bonding in a pure TGDDM and DDS system and, therefore, the peak 1720 cm⁻¹ results most probably from additives in the 934 resin. The obvious change of the spectra is that the 1720 cm⁻¹ band, which exists in the original dry specimen, decreases significantly after long-time immersion in water (9000 h) at different temperatures. As the immersion temperature rose, the 1720 cm⁻¹ peak decreased significantly. For the 90 °C specimen, the peak nearly vanished (Fig. 7.10-a). To substantiate that the change in peak height is caused by water sorption and not by a temperature increase, a sample of dry material was temperatureaged first at 60 °C for 2250 hours and, then, for an additional 250 hours at 100 °C. Subsequently, infrared testing was conducted on this temperature-aged specimen. The results (Fig. 7.10-f) indicated that 1720 cm⁻¹ peak did not change during the long-time. temperature-aging process, and, consequently, it was discerned that the decrease of the 1720 cm⁻¹ peak was due to the exposure of the specimens in the hygrothermal environment. When the 90 °C saturated specimen was completely redried by desorption of water at 100 °C for 250 hours, the 1720 cm⁻¹ peak did not recover. This finding shows that the change is irreversible and may be associated with additives or oligomers leaching out from the polymer matrix. Also, a new 1666 cm⁻¹ band is caused by thermal aging is shown. This peak might be due to an oxidation reaction during temperature aging.



Fig. 7.11 Infrared spectra of epoxy 934 at different hygrothermal stages.

7.3 SUMMARY

Three types of bound water exist in moisture-saturated graphite/epoxy (T300/934) composites. Depending on the water/resin interaction and bound-state characteristics, these types are designated as Λ -bonded water, Γ -bonded water, and Θ -bonded water.

Λ-bonded water is described as physiosorbed water. Molecules of Λ-bonded water diffuse into the material and break the interchain bonds that exist initially in epoxy resin and form weak hydrogen bonds via Van der Waals type force. Most of Λ-bonded water is dispersed by interchain hydrogen bonds and only a small amount of Λ-bonded water is in a free-water state. The net effect of interchain bond breaking is increased mobility of the polymer chains and, consequently, enhanced matrix swelling and plasticization and lowering of the T₈.

Γ-bonded water is described as a chemisorbed water that interacts chemically with certain hydrophilic groups of resin matrix. The amount of Γ-bonded water is strongly dependent on immersion temperature and time. Γ-bonded water may form secondary crosslinking with the hydrophilic groups in the resin matrix. Consequently, it is contended that Γ-bonded water contributes to a slight increase in the T_g and matrix-dominated mechanical properties of the composites.

 Θ -bonded water is characterized by its propensity to be retained at surface defects, cracktips, and voids due to surface tension and capillary effects. Θ -bonded water contributes to excessive weight gain in the water sorption profile. Θ -bonded water is associated with anomalous, non-Fickian diffusion behavior.

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CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The major results of this dissertation are concluded as follows.

By water desorption measurement, desorption diffusivity calculation, amount of residual water determination, and NMR test, two types of bonded water were found in water-sorbed epoxy neat resins. Depending on the water-resin bonding characteristics, these types are designated as Λ -bonded water and Γ -bonded water. The Λ -bonded water is a physiosorbed water. The molecules of A-bonded water diffuse into the material and break the interchain hydrogen bonds that exist initially in epoxy resin and form weak hydrogen bonds via Van der Waals-type force. Most of physiosorbed water is dispersed and impeded by interchain hydrogen and only a very small (if any) amount of the physiosorbed water is in bulk (free) state. The Γ -bonded water is described as a chemisorbed water that interacts chemically with certain hydrophilic functional groups of epoxies. The amount of Γ -bonded water evolved of the total sorbed water content in the resin depends strongly on exposure temperature and time. These two types of bonded water influence hygrothermal phenomena in epoxy resins and in Gr/Ep composite materials. In addition, a third type of bound water was found

on the surface and near surface area of Gr/Ep composite. It is noted as Θ -bonded water. Θ -bonded water is characterized by its propensity to be retained at surface defects such as cracktips and voids due to surface tension and capillary effects. Θ -bonded water contributes to excessive water uptake, and, hence, immoderate water-induced weight gain in the composite material. Θ -bonded water is associated with anomalous, non-Fickian diffusion behavior.

- The variation of T_g of epoxy in a hygrothermal environment can be summarized as follows: i) the change of T_g does not simply depend on the water content in epoxy resin, ii) T_g is associated with the hygrothermal history of the materials, and iii) for a given epoxy system that maintains a constant maximum water content, the longer exposure time and higher exposure temperature cause higher T_g . An interpretation is given for T_g variation. Both physiosorbed water and chemisorbed water have an influence on T_g . The experimental T_g value is the combined result of the two mechanisms. Physiosorbed water decreases T_g and chemisorbed water tends to maintain T_g at its original value and in some cases slightly increases T_g . Physiosorbed water decreases mechanical properties via the breaking of interchain hydrogen bonds and by increasing of mainchain mobility. Chemisorbed water does not decrease mechanical property. In contrast, it may slightly enhance strength-related properties via the formation of secondary-bond crosslinking with hydrophilic groups in epoxy.
- Swelling is essentially proportional to water gain. Physiosorbed water shows a significant influence on swelling because of its ability to interchain hydrogen bonds.

Chemisorbed water also creates some swelling, but compared to physiosorbed water the effect is significantly smaller. Moisture-induced expansion in composite was measured in length (fiber direction), width, and thickness directions. Essentially, no expansion due to water absorption was detected in the fiber direction dimension. Significant dimensional changes resulting from moisture-induced expansion were observed in the width and thickness directions of the laminate. The thickness decrease of the specimen at high temperature was associated with surface resin dissolution and peeling.

Depending on the structural chemistry and processing conditions, epoxy resin systems exhibit a wide range of water saturation levels. Plasticization effects are quite different for different epoxy systems. High water-absorption epoxy shows a significant decrease of both modulus and strength when the epoxy resin is saturated with water. Moreover, the degradation is temperature dependent. Higher exposure temperature induces lower modulus and strength. Low water-absorption epoxy resins show no significant modulus change, but a slight decrease of strength is realized. The most significant hygrothermal effect for all epoxy systems, in general, is the large decrease of failure strain. This change is irreversible. Also, the failure strain decrease is exposure temperature dependent. The most likely cause is due to chain scission during the hygrothermal process. Moisture-induced degradation was quite evident for the Gr/Ep composite. The delamination fracture toughness of the T300/934 laminate was lowered by approximately 60 percent after sustained exposure to hygrothermal environment. Plasticization of the bulk matrix and the interface phase by sorbed water

influenced the reduction in fracture toughness. Water-induced plasticization caused resin softening and strength loss. Moreover, water tended to weaken resin in the vicinity of the fiber/matrix interface. The degrading effect of water in the Gr/Ep composite was manifested by preferential cracking along the weakened fiber/matrix interface. Persistent fracture mechanisms appeared to be interfacial cracking, debonding, and microcrack growth and coalescence in the plasticized matrix material.

Water sorption in graphite/epoxy composites exhibited both Fickian and non-Fickian diffusion behavior. Diffusion data showed that the time for the onset of non-Fickian behavior was inversely related to the exposure temperature. Anomalous (non-Fickian) behavior in the composite resulted from chemical modification and physical damage to the epoxy resin. Cracks, voids, and surface peeling were observed clearly by SEM and A crack/mass loss model favorably describes the optical microscopy. phenomenological behavior of Gr/Ep composite resulting from water absorption processes. At a low exposure temperature compared to T_g, there is minimal surface dissolution and physical damage to the material and the weight gain behavior is Fickian. However, with increasing exposure temperature, cracks, voids, surface peeling, and dissolution occur. Cracks can retain water which contribute to absorption behavior higher than the theoretical Fickian diffusion curve. Surface peeling and dissolution contribute to reduction in the specimen weight and, consequently, the weight change profile data falls below the theoretical Fickian diffusion curve. The resultant weight change profile represents the combination of these two factors: cracking and mass loss. Depending on the dominant mechanism, the experimental

moisture absorption vs. $t^{1/2}$ profile(curves) may either be higher or lower than the theoretical Fickian curve.

8.2 RECOMMENDATIONS

Many research methods, such as desorption measurement, desorption diffusivity determination, the amount of Γ -bonded water change, and NMR test, have been used to reveal the nature of water in epoxy resins. All the results suggested consistently that there are two different types of bonded water involving the water sorption in epoxy resins. But some key knowledge is still unclear and more effort should be pursued.

- Activation energy at both physiosorbed and chemisorbed water desorption stages needs to be determined. The determination of the activation energy will give a strongest and direct proof of the presence of the two bonded water. Temperatures of 40, 50, and 60 °C are suggested to determine physiosorbed water activation energy and temperatures of 120, 130, and 140 °C are recommended to determine chemisorbed water activation energy. Also, more experimental data should be collected in chemisorbed water desorption stage so that more precise desorption diffusivity can be obtained.
- An epoxy system with non-amine hardener is suggested using for water absorption and desorption measurement. Chemisorbed water is supposed bonding with hydrophilic group in epoxy resins. If there is no hydrophilic group in the material residual water should not exist. At low temperature all sorbed water can be removed easily and

quickly. This experiment will reveal very important information and provide direct evidence that the residual water is due to hydrophilic group of the material.

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